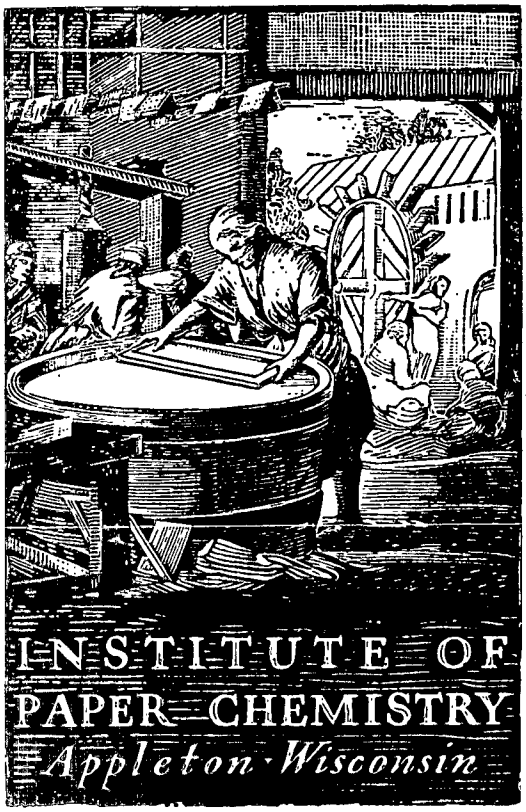

PROMOTION OF ALKALINE DELIGNIFICATION (AQ). INHIBITION OF LIGNIN CONDENSATION REACTIONS BY ANTHRAHYDROQUINONE; FORMATION AND CHEMISTRY OF QUINONEMETHIDE–ANTHRAHYDROQUINONE ADDUCTS

Project 3370

Report Two

A Progress Report

to

MEMBERS OF THE INSTITUTE OF PAPER CHEMISTRY

JUNE 2, 1980

THE INSTITUTE OF PAPER CHEMISTRY

Appleton, Wisconsin

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SUMMARY

The recent literature on anthraquinone (AQ) pulping and on mechanistic aspects of AQ's effects on carbohydrates and lignin (models) is reviewed. This is intended to supplement Report One — A Literature Review.

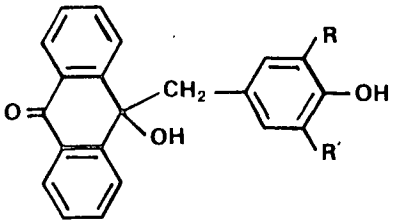
Addition of catalytic amounts of AQ to alkaline wood pulping systems cause an acceleration in the rate at which lignin is removed from the wood chips. This increase in delignification rate may be a result of AQ or anthrahydroquinone (the reduced form of AQ and abbreviated as AHQ) acting on the lignin fragmentation process, lignin condensation process, or both. In the fragmentation process macromolecular lignin polymers are degraded to water soluble lignin fragments. In the lignin condensation process water soluble lignin fragments recombine to give new lignin polymers. A retardation of the lignin condensation process would aid the delignification process. The impetus for much of our early research on Project 3370 was to establish what effects AQ or AHQ had on lignin condensation reactions.

One approach taken was to examine the behavior of an isolated, intact, lignin. Gel permeation chromatography (GPC) was used to analyze the molecular weight distributions of dioxane lignin and the products of cooking dioxane lignin with aqueous NaOH, NaOH/AQ, NaOH/glucose and NaOH/glucose/AQ. The cooking procedure apparently caused condensation reactions to occur since the profiles of the cooked

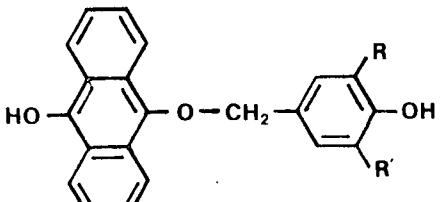
products showed a greater level of high molecular weight components than was present in the original dioxane lignin. The shift to higher molecular weight components was the least with the AQ/glucose run, suggesting that anthrahydroquinone (AHQ) suppresses condensation reactions. The virtues and pitfalls of GPC as applied to lignin analyses are discussed.

A second approach to the study of condensation reactions was to examine the reactions of vanillyl alcohol, a simple model lignin, in alkali with additives present. Vanillyl alcohol was heated with base at 173° for 2 hr in a titanium bomb and the product analyzed by GPC, gas chromatography (GC), nuclear magnetic resonance (NMR) and GC-mass spectroscopy. Several condensation products of the dimer and trimer type were characterized. AHQ, but not AQ, suppressed the formation of dimers and trimers when added to the vanillyl alcohol cooks. These results imply that AHQ is capable of retarding typical lignin condensation reactions.

Recent literature results from several laboratories suggested that AHQ was also capable of promoting fragmentation processes in model lignin compounds. Since both lignin fragmentation and condensation reactions are postulated to involve reactive lignin intermediates known as quinonemethides (QMs), it seemed reasonable that AHQ somehow interacted with such species. This logic led us to examine the reactions of anthrahydroquinone dianion, AHQ^{-2}, with QMs. The dianion was generated from dithionite treatment of AQ and mixed with compounds capable of forming QMs in aqueous base solution. Excellent yields of additional compounds, i.e., QM-AHQ adducts, were isolated. The adducts were characterized by elemental analysis, infrared, NMR and ultraviolet spectroscopy and shown to have the following structure:

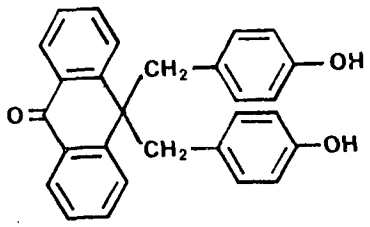


The dianion of AHQ has been treated with a variety of substrates in an attempt to understand the types of chemistry that may be occurring in pulping systems. The substrates which were reactive toward AHQ^{-2} were: QMs, conjugated ketones and aldehydes, and alkyl halides. Simple ketones and aldehydes did not react. O-Alkylated adducts, like the one shown below, have been postulated to be present in pulping systems which contain AQ. However, even using a variety of conditions and short reaction times, we were never able to observe any O-alkylated adducts. Apparently, if they exist at all, O-alkylated products are quite stable.



The reaction between AHQ^{-2} and a QM to give a QM-AHQ adduct has been shown to be reversible at temperatures of 60° and above. Evidence for this has been found in several reactions. Interestingly, if the adducts were heated at 100° in a nitrogen atmosphere, we observed the nearly quantitative yields of AQ and a 2:1 QM:AHQ adduct (see structure below). Both the 1:1 and 2:1 adducts

were unstable in alkali at pulping temperatures (173°), giving rise to AQ and a host of decomposition products.



Speculation is presented as to what roles QM-AHQ lignin adducts might play in the promotion of lignin fragmentation and retardation of lignin condensation reactions during the pulping of wood.

Pulps and liquor samples were analyzed for AQ by GC and polarography. The advantages and disadvantages of the two methods are compared. Pulps were found to contain 2-4% of the original AQ added to alkaline digestion of wood; liquors contained 30-50%. The rest of the AQ is presumed to be bound to water soluble lignin; this is what other investigators have found.

A characteristic of anthraquinone pulping is higher than normal pulp yields. Work outside the Institute has established that AQ oxidizes carbohydrates, producing aldonic end groups on the polymer materials. There is less "peeling", i.e., end-wise loss of sugar monomers from the carbohydrate polymer, when AQ is present. We briefly examined the reaction of cellobiose, a model carbohydrate, with alkali and anthraquinone monosulfonate (AMS) at 100° and 150° in a fast flow reactor in hopes of quantifying the relative rates of oxidation *vs.* peeling of cellobiose. Very few differences in the content of disaccharide components were observed between control runs (containing no AMS) and AMS runs. At 100°,

the AMS runs showed high levels of deoxypentonic acids and low levels of isosaccharinic acids; the control runs showed just the opposite.

The Cannizzaro reaction represents a way in which an aldehyde can be converted to an acid in an alkaline medium. Anthraquinone could be acting as a Cannizzaro catalyt when oxidizing sugar aldehydic groups to acids. To test this hypothesis, we briefly examined the influence of AQ and AMS on the Cannizzaro reaction of benzaldehyde; the results were encouraging, but inconclusive.

INTRODUCTION

This report will describe all of the pertinent research areas which have been investigated under Project 3370 since its inception. Some areas were quite fruitful in the knowledge generated, other areas not. Report One was a literature survey. In order to keep the reader abreast with the fast pace of anthraquinone pulping research, I have included in this Introduction Section all the published articles, excluding patents, dealing with this subject of anthraquinone pulping since its introduction in 1977 until now. This includes articles received at the Institute before February 1, 1980 and covers nearly all the 1979 literature.

The main emphasis and accomplishments of Project 3370 have concerned the effects of anthraquinone (AQ) and/or anthrahydroquinone (AHQ) on lignin condensation reactions and the formation of adducts between quinonemethides and AHQ. Consequently, these subjects will be discussed in the greatest detail. Because of its pertinence to the subject of this report, the master's thesis of Tom Brown (IPC, June 1979) on the effects of AQ on the molecular weight distribution of loblolly pine dioxane lignin during alkaline cooking will also be discussed.

Two other research areas, which were investigated under Project 3370 but do not fit the general theme of this report, will be included in Appendix Sections. The one area, under the direction of Ron McKelvey, involved the analysis of AQ in pulps and liquors by gas chromatography and polarography. The other area involved a brief study of the reactions of cellobiose and benzaldehyde with anthraquinone monosulfonate (AMS) and utilized some special equipment and experience available at the Institute.

The goals of this project are to develop an understanding of the mechanism of action of AQ in alkaline pulping systems and to use this knowledge to improve existing processes.

PULPING STUDIES

Studies on the application of AQ and related additives to soda and kraft pulping have been reported by several groups (1-30) and reviewed by many (31-40). The results of these studies indicate that catalytic quantities of AQ, when added to a soda or kraft pulping process, lead to increased pulp yields and faster reaction times.

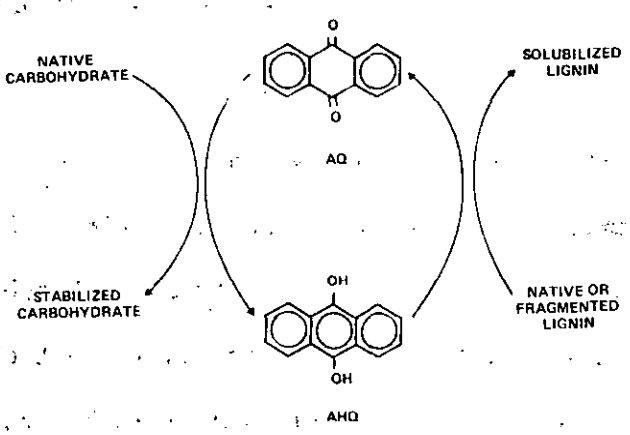
As a pulping additive, AQ can be used to decrease one or more of the following: (1) cooking times and, thus, increase production, (2) cooking temperature, (3) some alkali requirements and (4) sulfidity and, thereby, some of the pollution problems of the kraft process. For example, without changing sulfidity levels, kraft-AQ gives about a 2% better yield than plain kraft, with 13% less cooking time.

At least initially, it appears that AQ will be used in applications directed towards "debottlenecking" problem areas in existing mill operations. The prospects of replacing kraft pulp with soda/AQ pulp do not look promising at this time due to the cost of AQ and the somewhat inferior strength properties of the soda-AQ pulp.

Considerable effort is being directed at determining the bleachability of soda- and kraft-AQ pulps (41-44). At this time there does not appear to be any harmful effects of AQ to the environment or humans (45-49).

REDOX CYCLE PROPOSAL

Considerable research in the past few years has led to the proposal that anthraquinone and its reduced form, anthrahydroquinone, enter into a redox cycle (Fig. 1) with the two principal constituents of wood, carbohydrates and lignin (50-52). The redox cycle mechanism has AQ oxidizing carbohydrates, leading to stabilization of the carbohydrates and increased yields, and AHQ reducing lignin and somehow increasing the rate of delignification.



Fiqure 1. Proposed Mechanism of Action of Anthraquinone

CARBOHYDRATE CHEMISTRY AND AQ

The strong alkali, used in soda and kraft pulping, has detrimental effects on carbohydrate yields and chain length. From the moment that wood is placed in a digester with strong alkali, a reaction takes place, known as "peeling", that results in the successive loss of reducing sugar end groups from the polymeric chain (53). This reaction is believed to be the major cause of pulp yield losses.

At higher temeratures the alkali can also cause scissions of the polymeric carbohydrate chains, leading to shorter chain lengths and, thus, losses in pulp strength.

A favorable alkali-carbohydrate reaction, which occurs concurrently with the peeling reaction, but much less frequently, is the "stopping" reaction (53). Here, the reducing end groups are converted to metasaccharinic acid end groups which are stable towards the peeling reaction.

Anthraquinone adds another dimension to these carbohydrate reactions. In comparison to control runs, alkaline degradations of carbohydrates in the presence of AQ show decreased levels of isosaccharinic acids (the peeling reaction by-product) and, following hydrolysis, increased levels of aldonic acids (54-62). The latter arise because of an AQ oxidation reaction of the terminal sugar units (RCHO → RCO_2H). These reactions are outlined in Fig. 2.

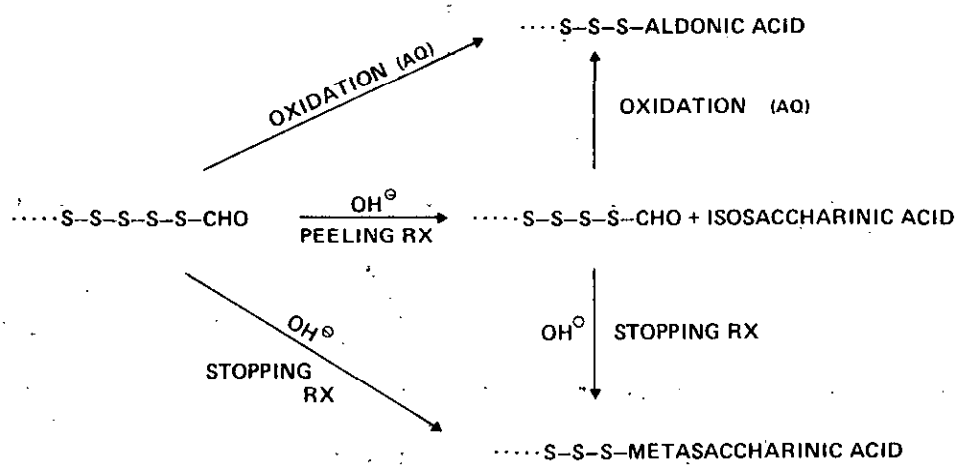


Figure 2. The Proposed Reactions of Carbohydrates in Soda/AQ Pulping

The pulps produced in soda/AQ wood cooks are generally weaker than similar kappa number pulps obtained from the kraft process (63,64). This result suggests that AQ might promote carbohydrate chain cleavage reactions (25,28,65). Recent studies at The Institute of Paper Chemistry have, in fact, shown that AQ resembles oxygen/alkali in its effect on amylose degradation; both give high carbohydrate yields and chain cleavage (65).

Another explanation for the higher pulp yields in the presence of AQ can be related to another facet of anthraquinone chemistry, namely its ability to increase the delignification rate. The shorter cooking times, lower temperature and less alkali frequently employed in AQ cooks all favor less carbohydrate degradation. In summary, the increased pulp yields associated with AQ pulping can be attributed to a combination of less severe cooking conditions and an oxidative stabilization of carbohydrate end groups; the poorer pulp strengths may be a consequence of AQ promoting chain cleavage reactions.

LIGNIN CHEMISTRY AND AHQ

The delignification of wood is thought to involve two key reactions: (1) the fragmentation of the lignin polymer into smaller water soluble material — desirable — and (2) the recombination of small lignin fragments (condensation) into insoluble lignin or lignin-carbohydrate materials — undesirable. A simplistic representation of these two reactions is given in Fig. 3.

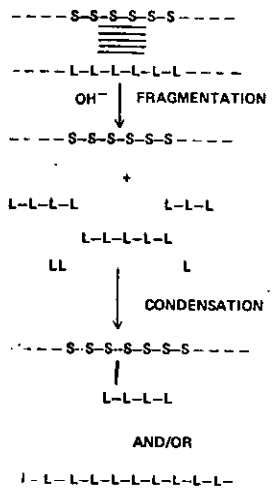


Figure 3. The Delignification Process, in Which Carbohydrates are Represented by Repeating Sugar(S) Units and Lignin by Repeating L Units

The key to lignin fragmentation reactions is the cleavage of the β-aryl ether linkages of lignin (Fig. 4) (66,67). Conceivably, these linkages could be cleaved directly by base *via* β-displacement, α,β-elimination or epoxidation reactions (Fig. 5). The phenolic materials which are naturally present in lignin or are produced by chain cleavage processes and possess appropriate leaving groups on the α-carbon can give rise to quinonemethide (QM) intermediates (Fig. 6). Quinonemethides are very reactive species, quite prone to attack by nucleophiles on the α-carbon, regenerating a phenolate ion. Although their concentration in solution will be low at any given time, quinonemethides have been postulated to account for a great number of lignin reactions (66,67).

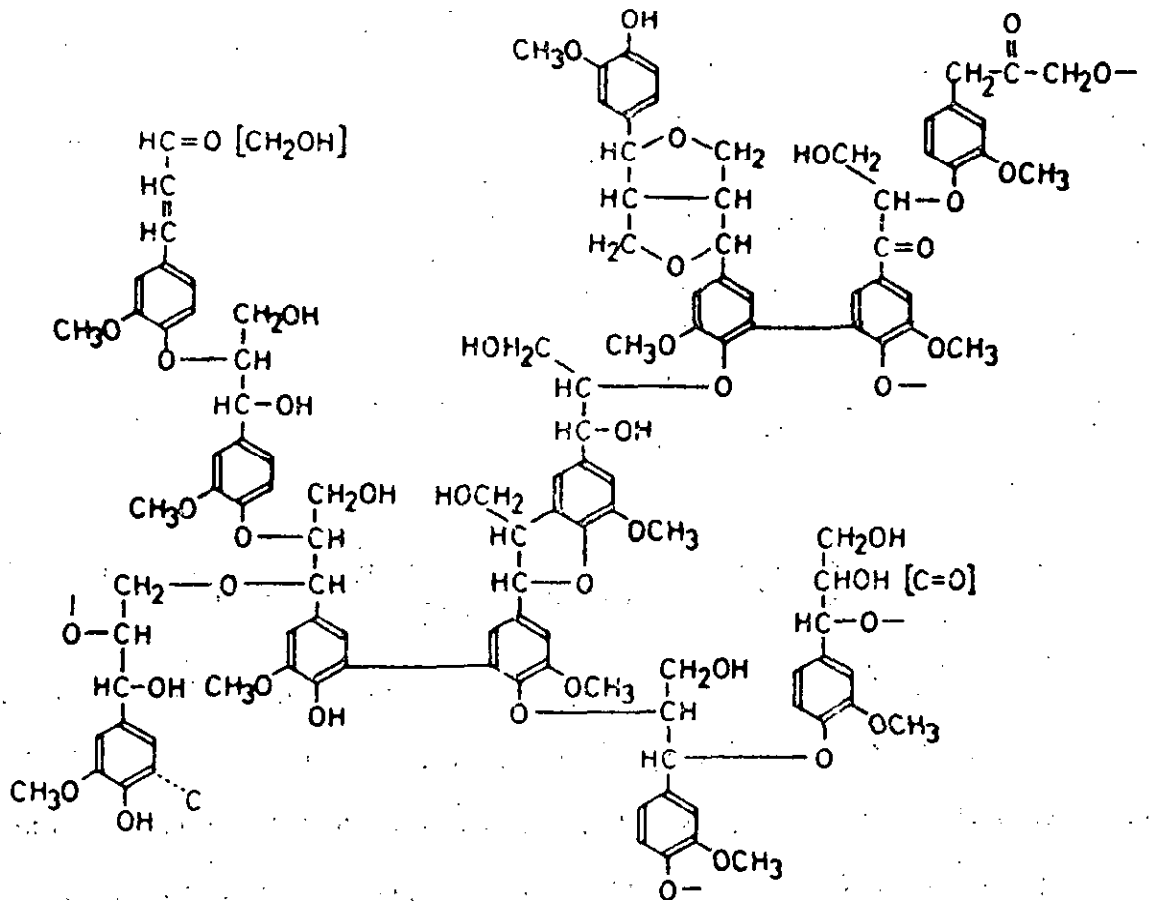


Figure 4. A Representation of Part of the Structure of Softwood Lignin

Figure 6 outlines two reactions of QMs with hydroxide ion. One reaction results in a stabilized lignin unit, the other in fragmentation. The latter is somewhat retarded by the presumed low acidity of the α-hydroxyl group in a molecule which is already extensively charged.

The sulfide ion, which is present in the kraft process, offers a new pathway for lignin fragmentation (Fig. 7). This ion is an excellent nucleophile,

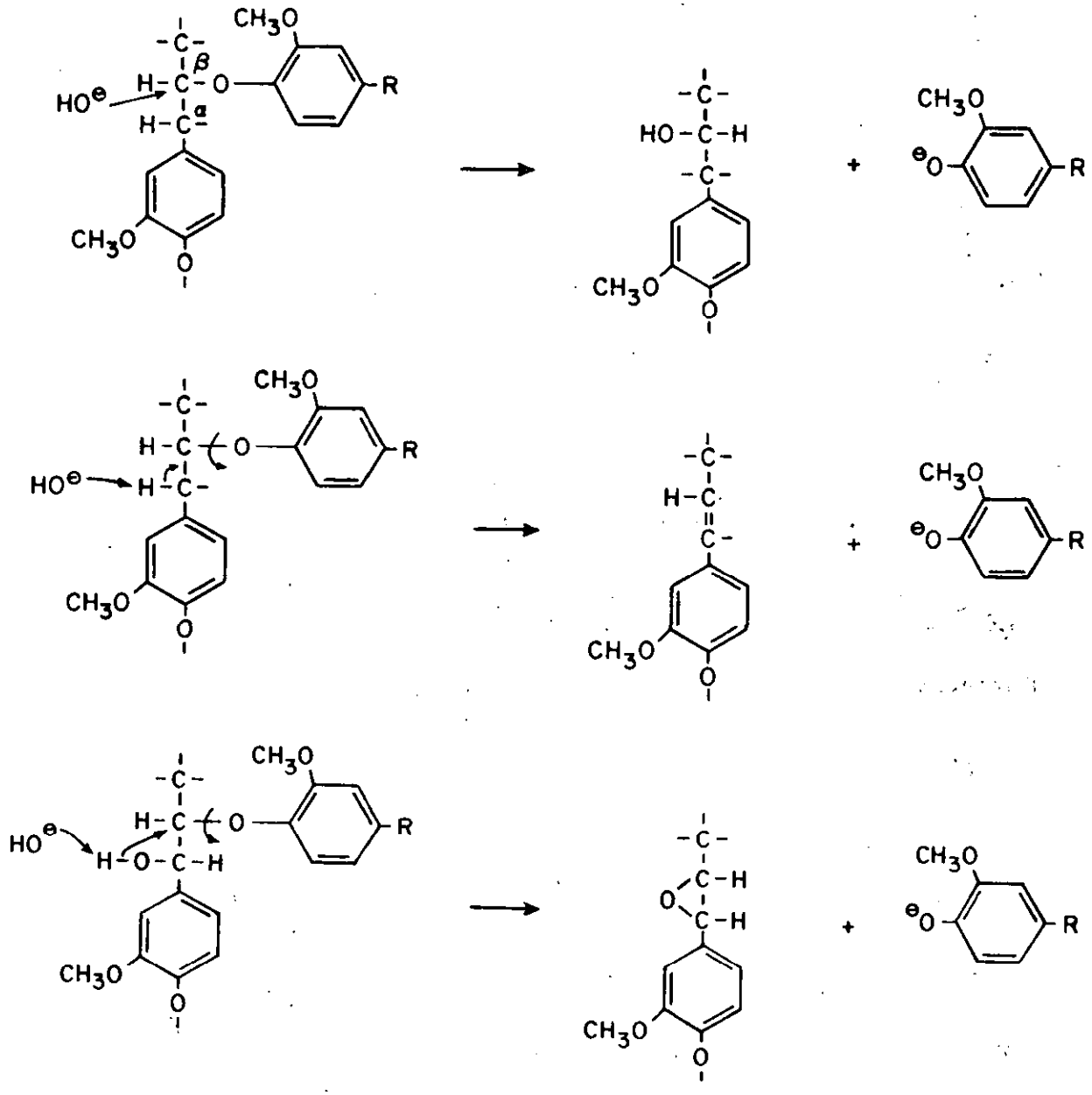


Figure 5. Chain Cleavage of Lignin by Alkali

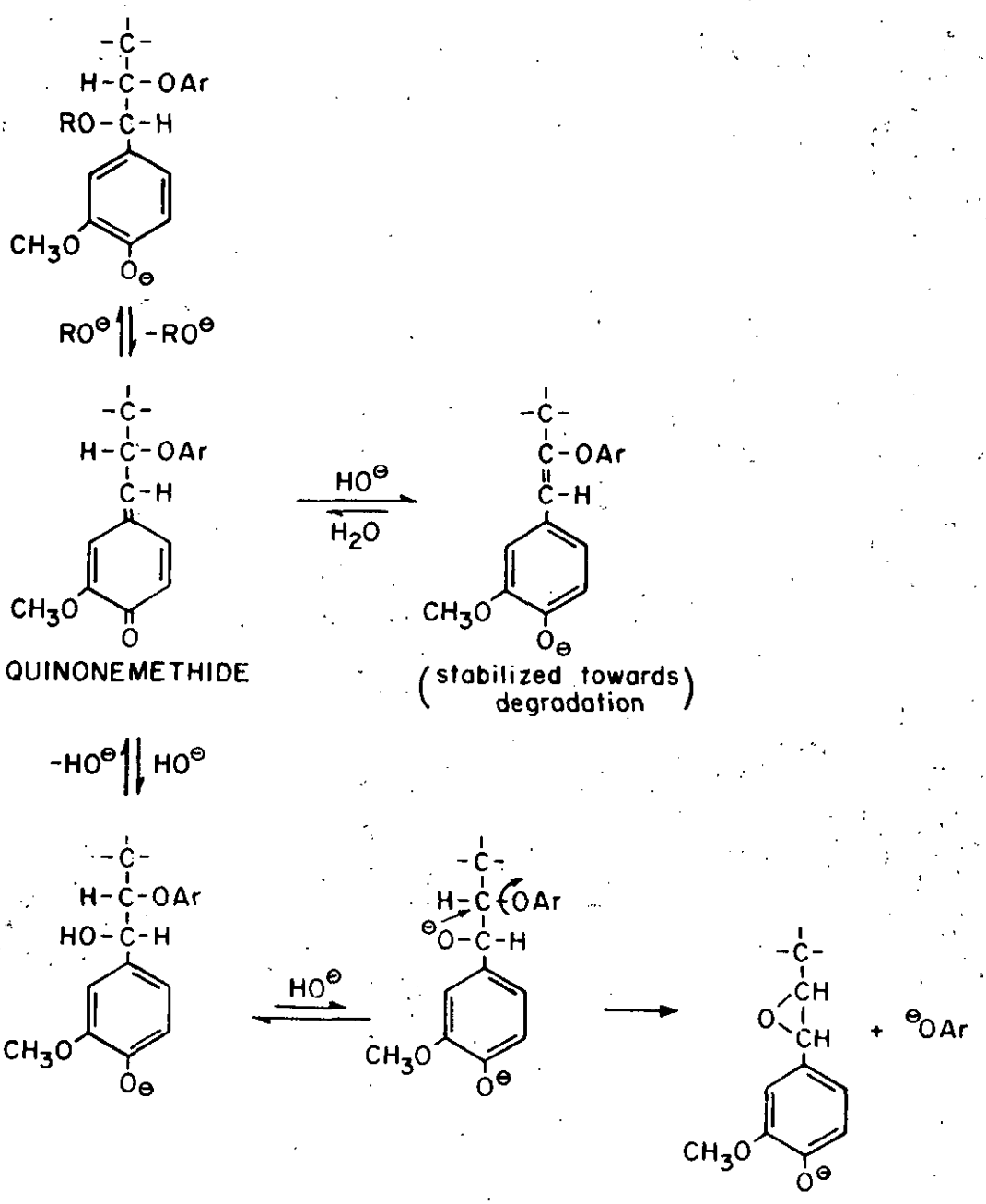


Figure 6. End-wise Cleavage of Lignin by Alkali

meaning that it will be much more reactive than hydroxide in (a) attacking QM intermediates and (b) displacing β-aryl ether substituents. Another factor which could account for greater efficiency of sulfide in promoting delignification is the greater acidity of RSH groups relative to ROH groups.

How does anthrahydroquinone fit into this chemisty? The evidence is fairly convincing that it is AHQ, rather than AQ, that is responsible for promoting delignification (52,68,69). Most of the studies reported so far on the mechanism of AHQ-lignin reactions have involved model compounds which resemble typical lignin monomers. These studies have shown that soda/AHQ is more efficient than straight soda at promoting fragmentation of models which are capable of forming quinonemethides having β-aryl ether substituents (70-73).

Figure 8 shows the results of one of these model studies (70). Anthrahydroquinone was generated *in situ* from AQ and pulp. Both kraft and soda/AHQ gave high yields of guaiacol (2), a fragmentation product, and low yields of the enol ether product 4. Straight soda gave just the opposite. The formation of 2-methoxy-4-vinylphenol (3) appears to be peculiar to the AHQ system and may be important to understanding the mechanism of action of AHQ.

Simultaneously, Landucci (74) at the Forest Products Laboratory in Madison, Wisconsin, and our group (75) at the Institute examined the reactions of AHQ with quinonemethides in an attempt to understand the AHQ-delignification process. The results of this type of research have provided new insights into the action of AHQ and constitutes a large portion of the discussions which follow in this report.

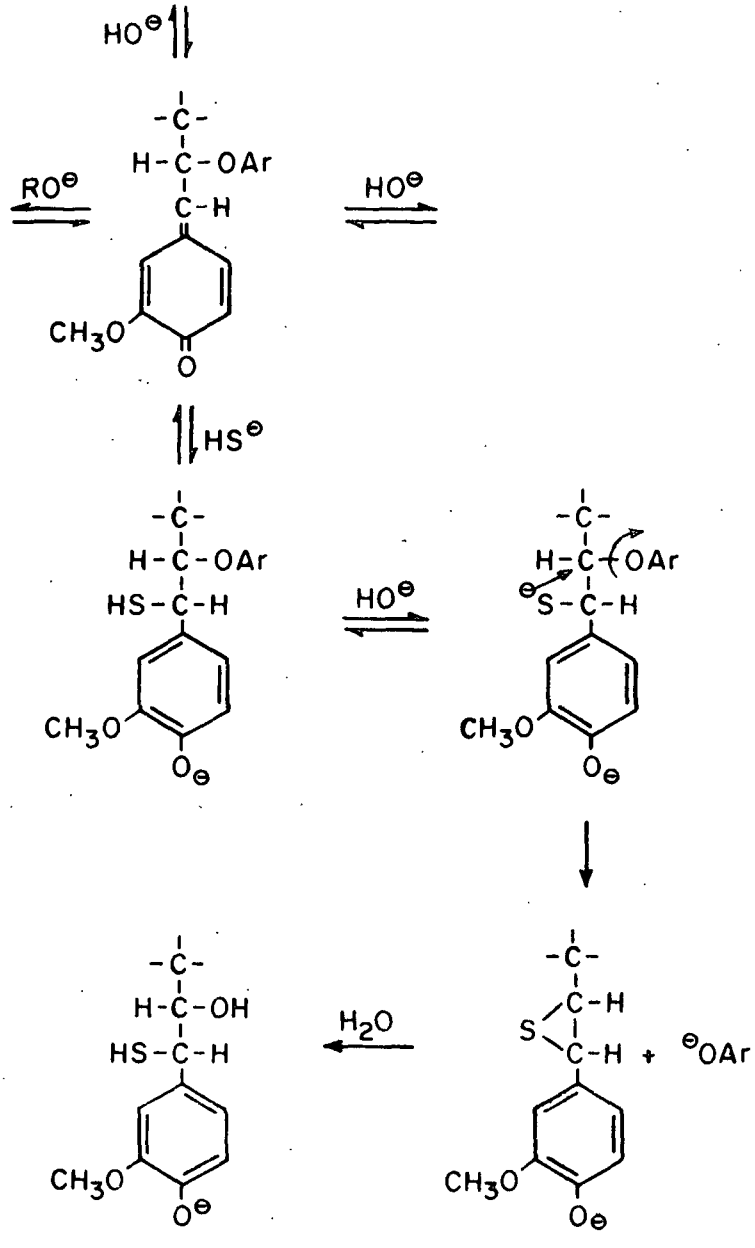
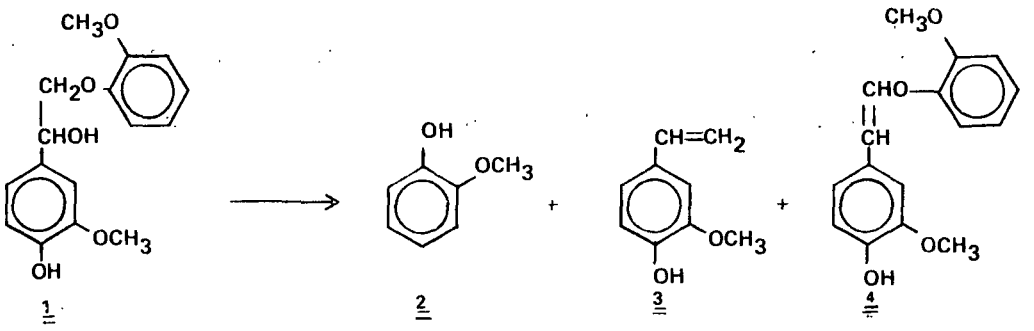


Figure 7. Effect of Sulfide on Lignin Degradation



CONDITIONS	YIELDS (%)		
SODA	23	0	45
SODA/AQ/PULP	76	32	3
KRAFT	79	TRACE	0

Figure 8. Alkaline Degradation of a Model Lignin (70)

The evidence for AHQ induced lignin fragmentation seems substantial. What about AHQ's effect on lignin condensation reactions? First, what is meant by lignin condensation reactions? Figure 9 depicts one of the prominent ways that lignin can condense with itself (66). Carbon-carbon bond formation between a phenolate ion and a QM results in lignin material which would be more resistant to alkali than native lignin. Condensation reactions of this type convert medium-to-small water soluble lignin into large insoluble material — essentially a reverse of the desired delignification reaction. The condensed lignin may, in fact, be largely responsible for "residual lignin", i.e., that lignin which is very difficult to remove during chemical pulping.

We have taken two approaches to studying how AHQ might affect lignin condensation reactions. One was to compare the molecular weight distributions obtained after heating "dioxane lignin" with alkali and alkali containing additives

(Brown's thesis work). The other was to examine a series of alkali-vanillyl alcohol cooks, some of which contained AHQ as an additive. The results of these investigations are covered in the next two sections of this report.

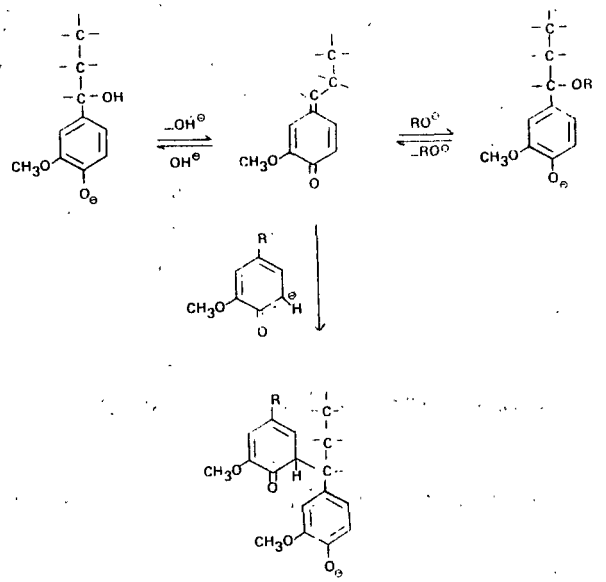
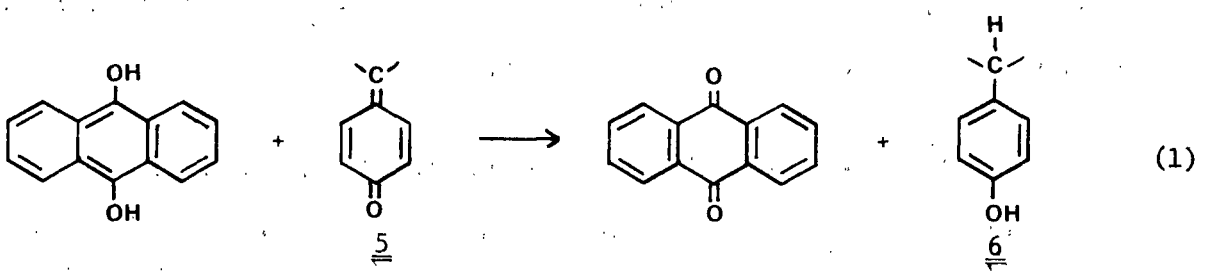


Figure 9. Lignin Condensation Reactions *via* Quinonemethides

The impetus for our work was an attempt to show that quinonemethides (5) could be reduced to phenols (6) by AHQ. A conversion of this type, Eq. (1), would lead to materials which should be much less prone toward condensation reactions.



(1)

FATE OF AQ

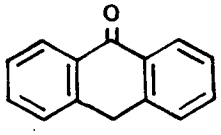
The detection of anthraquinone and its chemical by-products in pulps and liquors has been mainly accomplished by gas chromatography (GC), GC-mass spectroscopy (MS) (49,77) and polarography (78). The GC method of analysis generally supports the conclusion that only a few percent (ca. 5%) of the charged AQ is retained in the unbleached pulp (76,77). Since the original AQ levels are usually quite low, the levels of AQ in unbleached pulps are only about 1,000 ppm (77). The levels of AQ in bleached pulps are in the range of 0-5 ppm.

The majority of the anthraquinone appears in the liquor, (49,51,76-79) where it is partitioned between "free" AQ and "bound" AQ. The latter term refers to AQ which is tightly associated (probably via chemical bonding) with alkali-soluble lignin (51). Because of volatility problems, GC methods will most likely be unable to detect "bound" AQ. It is not surprising then that GC methods have only detected about 50% of the original AQ charge (76). The anthraquinone present in the liquors appears to present no significant biological problem (45-49).

Dence's detailed study of the black liquors obtained from AQ/soda cooks indicates that the major AQ components of the liquor are AQ and AHQ (49). There are, however, small amounts of reduction products, namely anthrone (7), anthracene (8), and 9,10-dihydroanthracene (9). Fullerton and Ahern have reported isolating a benzanthrone product 10 from AQ pulping liquors (79). Fullerton and Fleming have also isolated small quantitites of 2-vanillyl-anthraquinone (11) (80).

Fleming and coworkers have used polarography to analyze soda-AQ pulping liquor during the course of warming black spruce wood (78). Interestingly, they have shown that AQ is rapidly converted to AHQ above 95°. The concentration of

AHQ increases steadily until a temperature of 125° is reached, then the concentration decreases with further temperature increases. The total concentration of AQ and AHQ decrease at higher temperatures. In fact, after a warm-up period of 1.5 hr and 2 hr at 170°, only 40% of the originally charged AQ remained as AQ or AHQ. They interpret the rise and fall of AHQ during warm-up as support of a redox mechanism (Fig. 1) in which AHQ is formed by carbohydrate reactions at low temperatures and AQ is regenerated *via* lignin reactions at high temperatures; both species slowly decompose at high temperatures.



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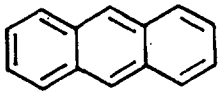

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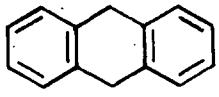

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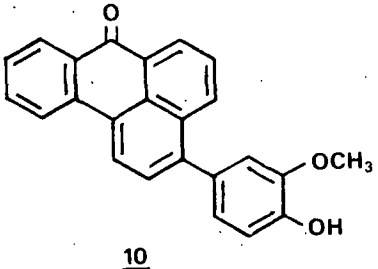

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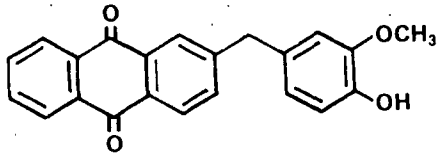


11

Farrington and coworkers (51) have used ^{14}C-labeled AQ to show that as a wood cook proceeds increasing amounts of AQ become bound to black liquor lignin. There are several other groups also studying the fate of AQ using labeling techniques; these studies should be quite informative.

MISCELLANEOUS

Kettunen and coworkers recently reported that AQ exhibits its catalytic effects on neutral and alkaline sulfite (81). Anthraquinone has also been used as an additive in the pulping of bamboo (82).

A comparison of yield and composition of tall oil from soda/AQ and kraft showed only minor differences (83). It is quite likely that the tall oil from soda/AQ will be of higher quality than the corresponding kraft product since the former should be void of the bothersome sulfur impurities which plague the latter. Work on establishing this point is in progress at the Institute (84).

Several studies have concerned the effects of AQ or AHQ on lignin degradation using intact or isolated lignin. Bruun and coworkers looked at the effect of AQ on the delignification of the tracheid cell wall (85). Molecular weight distribution studies have indicated that AQ-AHQ causes the production of lower molecular weight lignin (50,70,86,87) and less condensed lignin (88) when an isolated lignin is heated in the presence of alkali.

Werthemann has been involved in evaluating pulping additives and has shown that AQ, sulfide, and other effective additives exhibit a square-root concentration relationship with regard to effectiveness toward carbohydrate stabilization and rates of delignification (89). While some other additives appear as effective as anthraquinone, i.e., tetrahydroanthraquinone (16,19,61,71) and phenazine (23), cost and environmental considerations still favor AQ at this time. The fact that phenazine and compounds like this function as pulping catalysts has been correlated with the additive's ability to take on and give up electrons, i.e., their redox characteristics (90).

Gratzl and fellow workers have studied lignin models and concluded that both AQ and AHQ are reactive, suggesting that a redox cycle involving AQ, AHQ and lignin exists (91-93). Studies attempting to prove if resin acids are capable of entering into redox cycles with AQ and AHQ are also in progress (84).

CONDENSATION REACTIONS OF DIOXANE LIGNIN

Loblolly pine dioxane lignin of weight average molecular weight of approximately 11,000 (94) was heated with aqueous alkali, with and without additives present. The additives examined were AQ (10% by weight, relative to the dioxane lignin), glucose (100% by weight) and a glucose-AQ combination. Glucose is known to rapidly reduce AQ to AHQ; thus, a glucose-AQ mixture is a simple way to generate AHQ. Similar cooks were done with sodium sulfide present to simulate kraft pulping conditions.

After heating (173°) for 45 min, the reaction mixtures were cooled, acidified and freeze-dried. The molecular weight profiles of the dioxane lignin and the various products were compared by gel permeation chromatography (GPC) using a SynChropak GPC 100 column and dimethylsulfoxide (DMSO) as the solvent, Fig. 10 and 11. The molecular weight profile of the dioxane lignin by this method was in excellent agreement with the profile obtained by gel filtration through a Sephadex G-100 column (94).

All of the cooks produced lignin of higher molecular weight than the starting dioxane lignin. In the straight alkali system, the cook containing AHQ (Fig. 10, curve E) appears to produce the least amount of higher molecular weight, i.e., condensation products. The conclusions concerning the kraft cooks (Fig. 11) are not nearly so clear. The large excess of sodium sulfide used in these cooks may have masked the effects of the additives. Here, AQ appears to be the most effective additive for suppressing the formation of high molecular weight material.

The determination of molecular weight profiles of lignin material is quite difficult, primarily because of the nature of the lignin. Lignin has a large number of polar groups which can adhere strongly to column packings unless a very polar

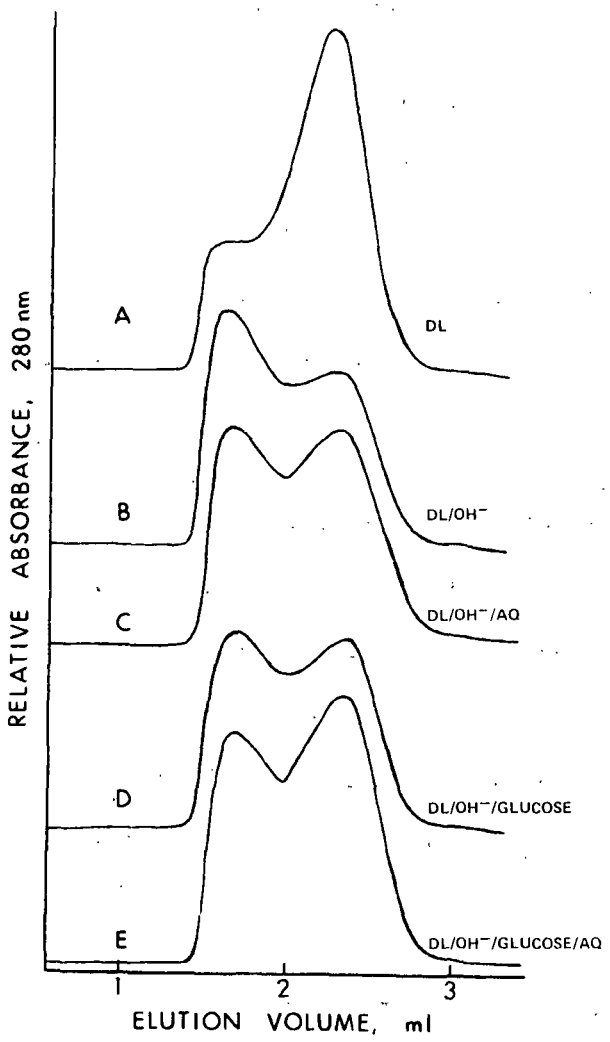


Figure 10. Gel Permeation Chromatograms of Dioxane Lignin (DL) and its Reaction Products with Alkali and Some Additives (88)

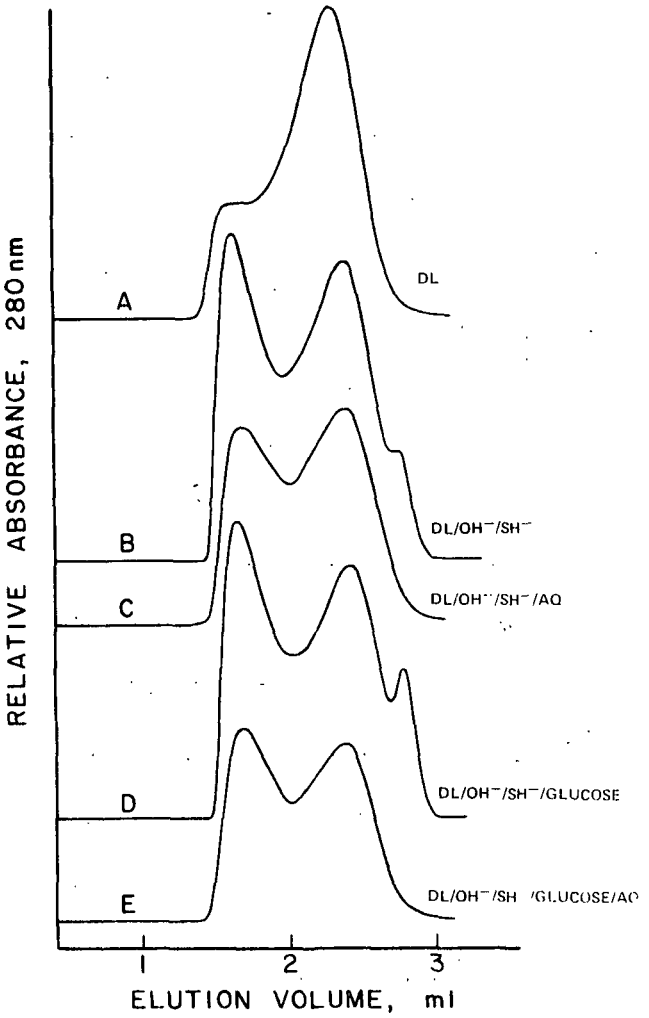


Figure 11. Gel Permeation Chromatograms of Dioxane Lignin (DL) and its Reaction Products with Alkali, Sulfide and Some Additives (88)

solvent is employed. Most GPC columns do not perform well when polar solvents are used. The SynChropak column used in this study has never been used to analyze lignin; its main application area has been in the analysis of proteins. The column adsorbed some lignin, giving distorted shapes, when 20% aqueous dioxane was used as the solvent during the analysis of the cook products. The columns appeared to function well with DMSO as the solvent.

Besides adsorption effects, GPC molecular weight profiles can be distorted by changes in chromophores when using an ultraviolet (UV) detection system. The assumption which is generally made is that the high molecular weight components absorb in the UV to about the same extent as the low molecular weight components. If, however, an additive, like AQ, causes additional chromophores in one, but not all molecular weight species, then the true molecular weight distribution will be distorted.

A third problem with GPC is that unwanted UV absorbing species can interfere with the analysis. All the AQ has to be removed from the samples since it is a strong UV-absorbing low molecular weight material. In filtering to remove AQ, some insoluble lignin could be lost. When acidifying to collect a lignin precipitate, the low molecular weight, water soluble, lignin will be lost. There is evidence that AQ becomes bound with the alkali soluble lignin found in soda/AQ pulping liquors (51). This should affect the UV absorbance of lignin in the low molecular weight range.

The point of all this discussion is that there are several pitfalls and assumptions made when employing GPC to the analysis of lignin molecular weight profiles. Great care must be taken to handle all samples alike. Even when done

right, adsorption effects and changes in UV absorption characteristics can distort the real picture. Firm conclusions are hard to draw from lignin GPC data.

Our results are consistent with already published results (50,70,86,87) which claim that heating high molecular weight lignin with alkali and AHQ gives smaller fragments than in the absence of AHQ.

CONDENSATION REACTIONS OF VANILLYL ALCOHOL

Another approach to the study of lignin condensation reactions is to examine the effects of alkali and high temperatures on a lignin model compound. Vanillyl alcohol (12) is about the simplest model available. After ionization in aqueous hydroxide, the phenolate 13 can reversibly form a quinonemethide 14 (Fig. 12). The quinonemethide, upon reaction with phenolate 13, could produce a dimer 15; depending on the type of bond formed, the dimer may be stable or in equilibrium with 13 and 14. Reaction of the dimer with more QM could give trimer, tetramer, etc., all the way up to small polymers.

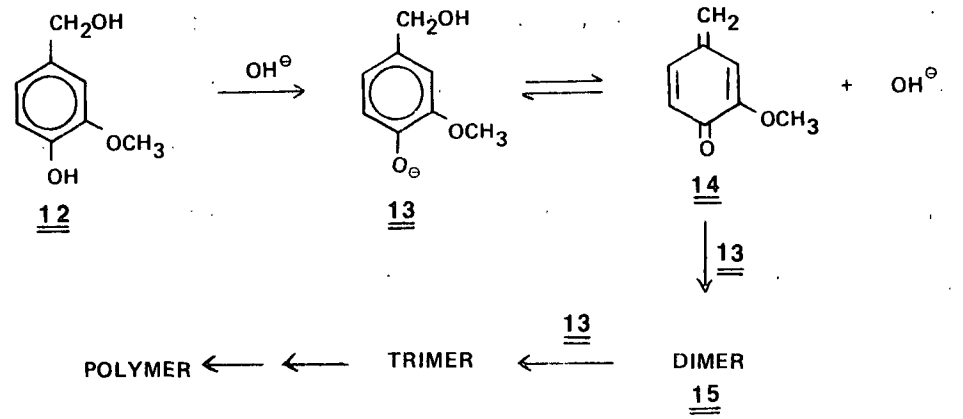
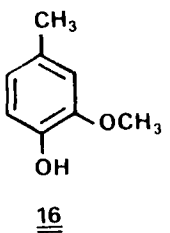


Figure 12. Possible Condensation Reactions of Vanillyl Alcohol

If AQ or AHQ were to interfere with these anticipated condensation reactions, one might observe (a) less polymer formation in the presence of the additives, relative to a control, and (b) reduction products like creosol 16.



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PROCEDURE

The vanillyl alcohol cooks were mostly done in titanium, sealed-tube reactors. Titanium was chosen to minimize the effects of trace metals on the reactions. Runs done in stainless steel reactors gave similar results, however. Fairly dilute solutions of vanillyl alcohol in 0.5N NaOH (154 mg in 30 mL of solution) which contained no additives, equal molar amounts of AQ, 3 molar equivalents of glucose, or combinations thereof, were heated at 173°C for 2 hr, under mild agitation. The reaction mixtures were then cooled and opened to the air; any AHQ should quickly be converted to AQ under these conditions.

Two different work-up procedures were employed at this point. The most frequently used procedure was to acidify the solution to a pH of approximately 6.0 and freeze dry. An alternate was to filter to remove the suspended AQ, acidify and collect the solid product. Analysis of the organic components in either the freeze-dried or precipitated products were qualitively the same. Figure 13 outlines these reactions.

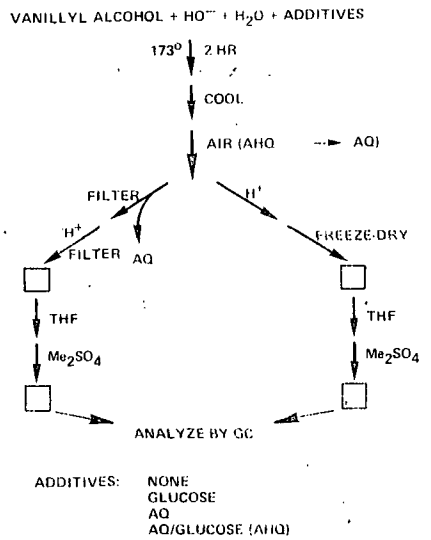


Figure 13. Outline of the Procedures Used in the Vanillyl Alcohol Reactions

GPC ANALYSIS

Analysis of the products by GPC was not successful. Columns which were capable of differentiating small polymers, i.e., combinations of μ-Bondagel and μ-Porasil, did not function properly with the solvents necessary to dissolve the products. The SynCrompak column used in Tom Brown's studies (88) showed very few differences between product samples; this column is not able to distinquish molecular differences below 5,000. Consequently, GPC analysis did not allow a distinction to be made as to the degree of polymerization in the control runs *vs.* the runs containing additives.

GC ANALYSIS OF DERIVATIZED PRODUCTS

Direct gas chromatographic (GC) analysis of precipitated products showed no creosol, the expected reduction product of quinonemethide 14 [see Eq. (1) p. 18]. The samples were extracted with hot tetrahydrofuran (THF), derivatized by methylation with dimethylsulfate and then analyzed by GC. Many more signals were present in the gas chromatograms of the derivatized products as compared to the underivatized materials. This was anticipated since methylation converts polar hydroxyl groups to more volatile ether groups. There were some major differences in the chromatograms of the derivatized cooked samples. These differences can be seen in comparing curves A-C in Fig. 14. The same amount of internal standard was present in each chromatogram.

The cooked sample which contained AHQ (actually AQ and glucose) showed substantially lower amounts of dimers and trimers. [Proof of these structures follows in subsequent sections.] The chromatograms of the control sample and the one containing only AQ as an additive had nearly identical levels of dimers and

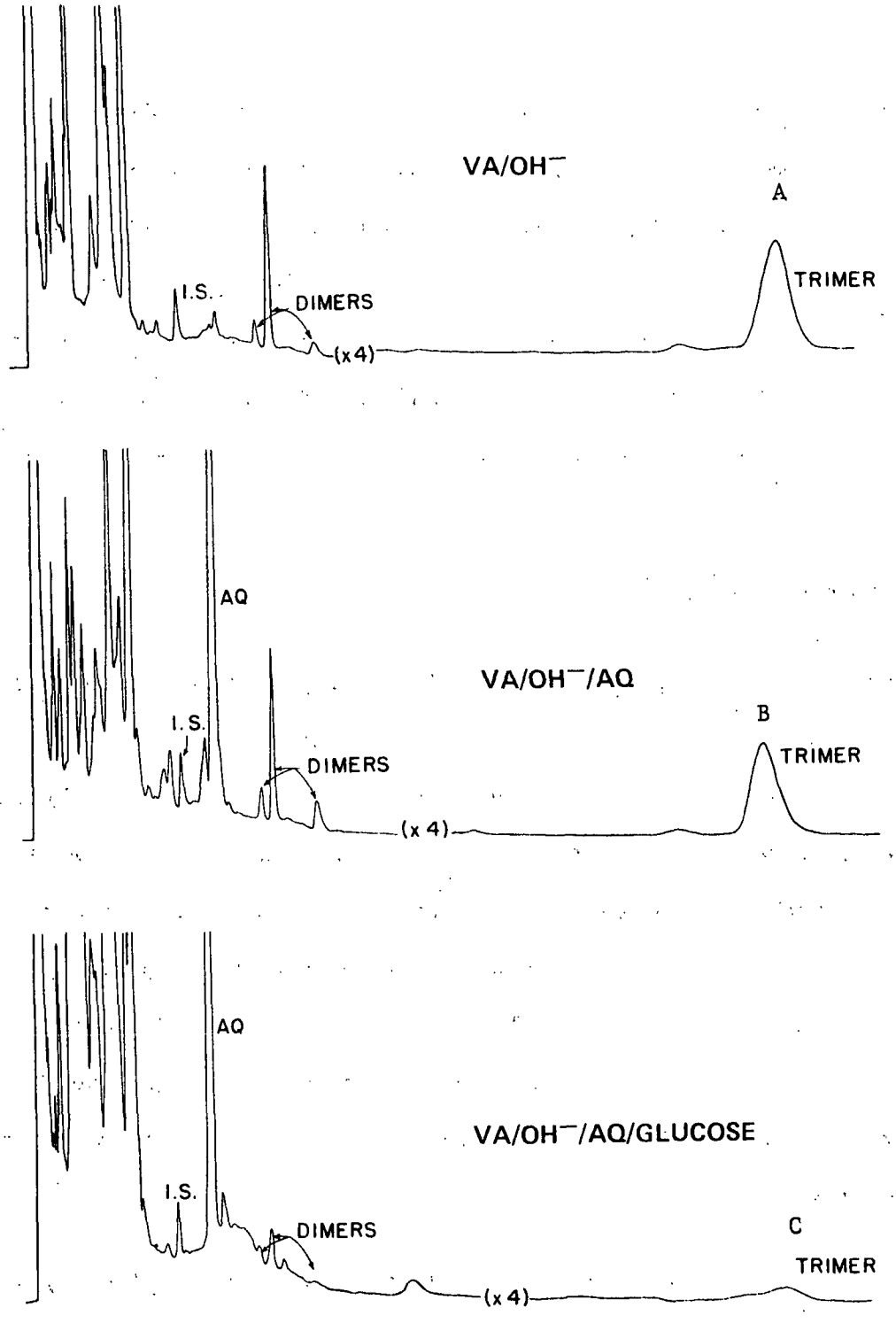


Figure 14. Reproductions of the Gas Chromatograms Obtained from Derivatized Products of Three Vanillyl Alcohol (VA) Cooks

trimers (Fig. 14 A and B). Approximate yields of 4 and 5% were calculated for the main dimer and trimer, respectively, in the control and AQ cooks by assuming a GC response factor of 1.0 for these materials, relative to the internal standard. When only glucose was used as an additive (GC curve is not shown in Fig. 14), the yield of main dimer and trimer was 3 and 1.3%, respectively. For the glucose/AQ additive mixture the yields were 1.5 and <0.5% for the dimer and trimer.

Although the GC method is not capable of showing low volatility products, such as tetramers to polymers, one could infer from the yields of the dimers and trimer that much less tetramers — polymers were produced in the AHQ cook relative to the control and AQ cooks. Apparently, *AHQ, but not AQ, is capable of depressing condensation reactions of vanillyl alcohol.*

The GC analyses of derivatized precipitated products were similar to those of the freeze-dried products, showing the same trends as just discussed. Glucose, alone, as an additive to the vanillyl alcohol cooks caused some decrease in levels of dimers and trimers, but not nearly to the extent of the glucose-AQ (i.e., AHQ) combination. One can speculate that glucose might capture quinonemethides in a reversible fashion, thereby, lowering the concentration of QM species and interfering with condensation reactions. It would also appear that AHQ is lowering the effective concentration of QM intermediates. But, what is AHQ diverting the QM to?

NMR ANALYSES

Analyses of the underivatized cooked samples by proton nuclear magnetic resonance (^{1}H-NMR) also showed that the control and AQ runs gave similar products, but the AHQ run produced additional aromatic signals in the 7.3-7.6 δ region and a sharp signal at 4.3 δ. Because of the method of workup, i.e., prolonged air exposure

and filtration, the new signals in the aromatic region cannot be attributed to AHQ. The spectra are shown in Fig. 15. Residual AQ can be seen in some of the spectra.

Condensation reactions should produce Ar-CH_2-Ar units, which will appear around 3.7-4.0 δ (95). This same region also contains $ArOCH_3$ signals. The aromatic signals for phenols and aromatic ethers occur in the 6.5-7.1 region of the spectrum. In comparing the spectra in Fig. 15, one can see that the AHQ cooked sample has less relative intensity in the $OCH_3/ArCH_2Ar$ region than the other samples. This is another indication that less condensation reactions have occurred in the presence of AHQ.

What is the cause of the signals in the 7.3-7.6 δ region which are so strong in the AHQ system and so weak in the others? This region is characterized by unsubstituted aromatics or aromatics which have no strong electron withdrawing or releasing substituents. Consequently, in our case this region would have to represent a vanillyl alcohol stripped of its aromatic oxygen or an AQ type molecule in which one or both carbonyl groups have been modified.

GC/MS ANALYSIS OF DERIVATIZED PRODUCTS

In order to characterize the components in the cooked products, we derivatized by methylation and submitted the resulting product to GC/MS (mass spectroscopy) analysis. A mass spectrum was recorded for each individual GC peak. For aromatic compounds, one expects to see fairly intense peaks corresponding to the molecular ion of the compounds. This is what was observed for AQ and the GC signals which had retention times longer than AQ. Generally speaking, the short retention time components did not display strong molecular ion signals in the MS. In fact, their spectra were dominated by low molecular weight ions and, consequently, structural

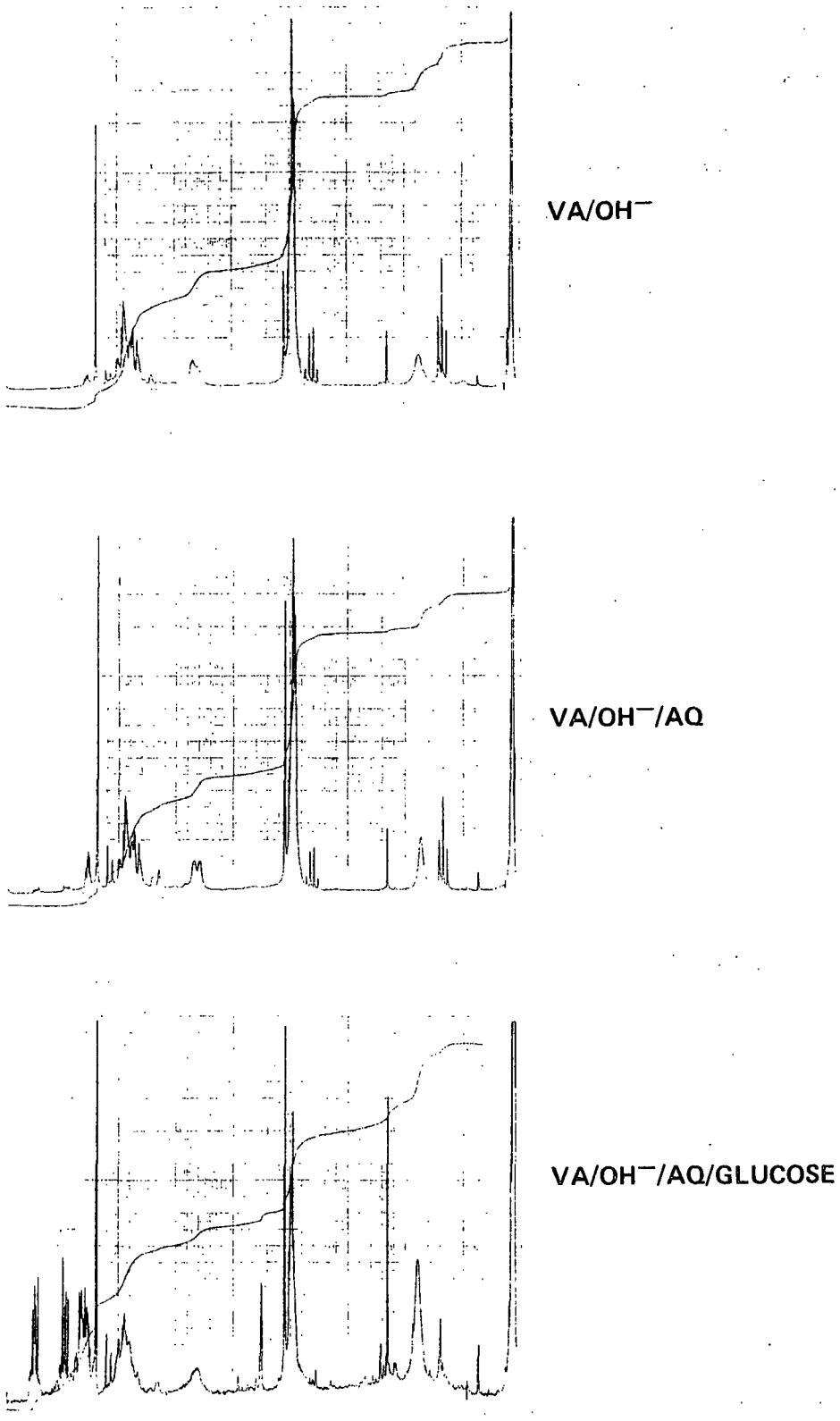
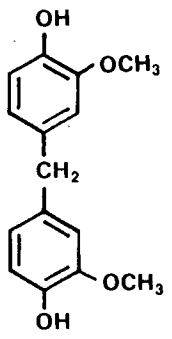


Figure 15. The ^{1}H-NMR Spectra of the Freeze-dried Vanillyl Alcohol Cook Samples

conclusions were not possible. One of the minor peaks in the AQ cook chromatogram appears to be methylated vanillin, by comparison to an authentic sample.

The three most prominent peaks directly following AQ in the gas chromatogram showed mass spectral molecular ions of 288, 288 and 332, which would correspond to methylated dimers of vanillyl alcohol (molecular weight 154). The molecular ions were quite intense, which is indicative of highly aromatic structures.

Based on the fact that a dimer of structure 17 had been previously isolated from a vanillyl alcohol alkali reaction (96) and its molecular weight after methylation would be 288, we assumed that one of the dimers corresponded to this structure. Compound 17 was synthesized (97), and methylated; the resulting product was identical to the most abundant dimer in both GC retention time and mass spectrum. The structure of the other mass 288 dimer is unknown at this time. The third dimer component probably corresponds to structure 19, since methylation of 19 would give a species of molecular weight 332.



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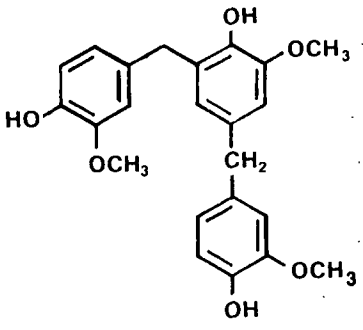

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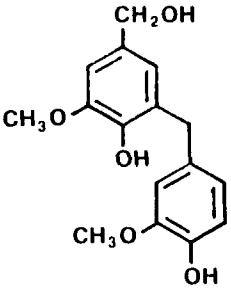


19

The long retention time component, referred to earlier as a trimer, was assumed to be the methylated derivative of structure 18, based on an intense molecular

ion at 438 and fragment ions at m/e 287 and 151. Small samples of the major dimer and trimer were obtained by preparative GC. The NMR spectrum of the dimer matched that of the synthesized dimer. The NMR of the trimer closely resembled that of the dimer, with principal absorptions at 6.5-6.8 (aryl), 3.8-4.0 (OCH_3 and $ArCH_2Ar$) and 3.7 δ (OH).

Very recently, Yoon and coworkers (98) reported that vanillyl alcohol condenses with itself at 100° in the presence of base to give a mixture of two dimers (12% and 3%), a trimer (25%), a tetramer (10%) and a pentamer (5%). The products were isolated by exhaustive column chromatography. The structure of the components, together with their acetate derivatives, were characterized by spectral means and elemental analysis. The components isolated corresponded to: major dimer 17, minor dimer 19, trimer 18 and a tetramer and pentamer which were analogs of 18.

The differences in yields of condensation products between Yoon and coworkers (98) and ourselves could be related to (a) assumption made by us with regard to GC response factors and (b) differences in reaction temperatures. Concerning this latter point, when the quinonemethide of vanillyl alcohol, i.e., structure 14, was generated at 60° in alkali [a reaction which will be discussed in more detail later], the yield of dimer 19 was quite high.

Probable mechanisms for the formation of dimer 17 and trimer 18 are shown in Fig. 16.

COOKS WITH DIFFERENT LEVELS OF AQ

In the vanillyl alcohol reactions described so far in this section, we used equal molar amounts of AQ (or AHQ) and vanillyl alcohol. What would happen if

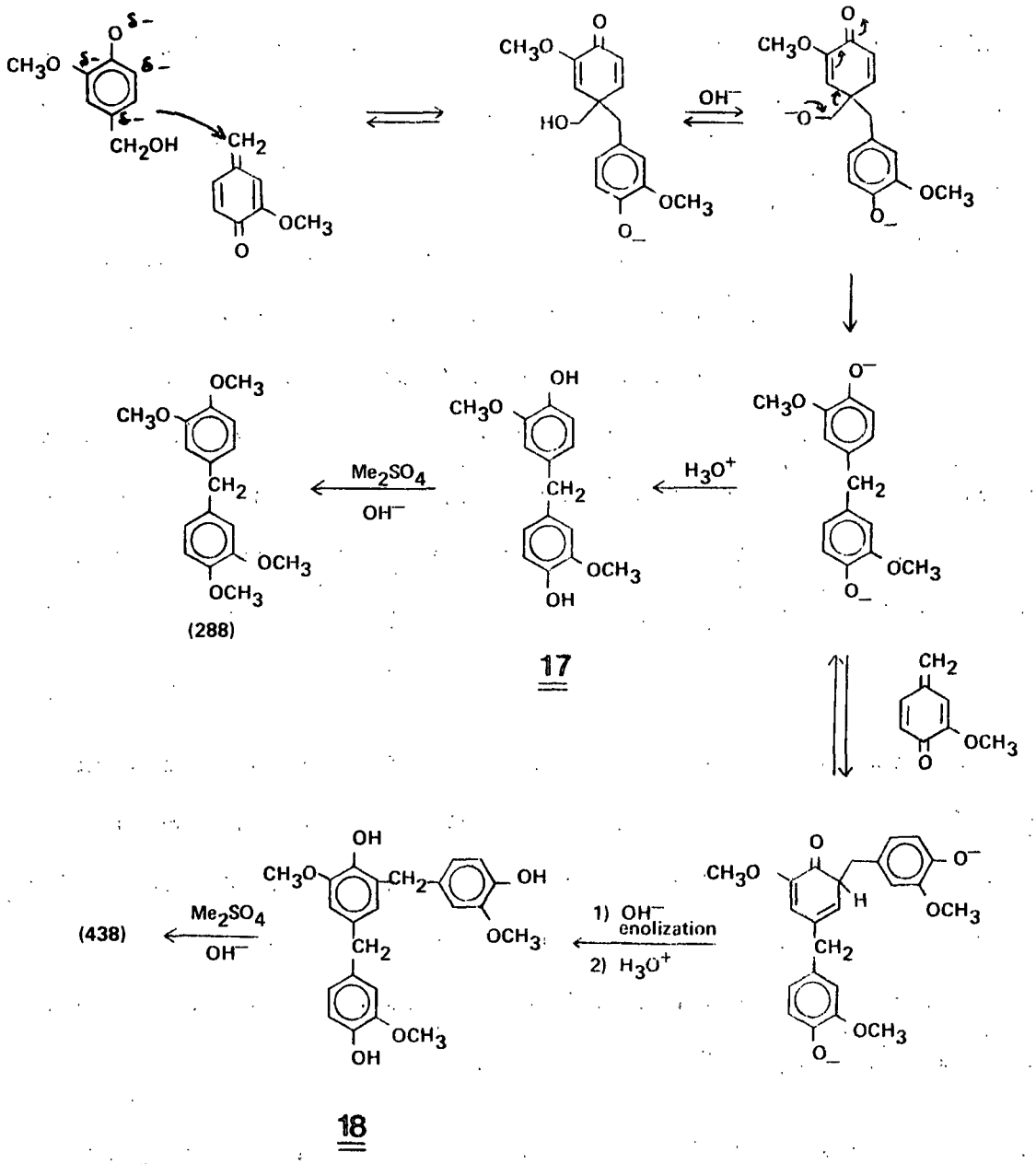


Figure 16. Probable Mechanisms of Formation and Structures for the Major Vanillyl Alcohol Condensation Products

low levels of AHQ were used? To answer this question we repeated the vanillyl alcohol (VA) cooks at various levels of AQ in an inert atmosphere.

Since glucose itself affects VA condensation reactions to a limited extent, an alternative way of generating *in situ* AHQ was sought. The most obvious way was the reaction of AQ with sodium dithionite. The reactions could be set-up with 1:1 ratios of VA and AQ and varying levels of dithionite. A control set of cooks, containing VA, alkali and various levels of dithionite, showed, however, that dithionite was excellent at retarding VA condensation reactions. This method had to be abandoned. A set of VA cooks were then performed in which an excess of glucose was present and different levels of AQ were added.

The data are given in Table I. The areas of the GC signals corresponding to the major dimer and trimer products and to an addition compound of AHQ and a quinonemethide (discussed in the next section) were compared to the area of an internal standard signal (equated to 1.0). Most of the decrease in dimer and trimer levels occurred with just a 2.5% level of AHQ; larger amounts of AHQ, however, led to decreased levels of condensation products and increased levels of "adduct". Another trend was also quite apparent, namely, the level of trimer fell off more rapidly than the dimer. Presumably, this is a consequence of having consecutive reactions.

The dramatic effect of low levels of AQ on the VA condensation reaction suggests a (redox) catalytic action. The question is what species is present to complete the redox cycle. Glucose is known to be rapidly consumed by warm alkali. Possibly, the VA-AHQ reactions are very rapid and are, thus, able to benefit from unreacted glucose. Maybe glucose by-products play a role.

TABLE I

VANILLYL ALCOHOL COOKS[a]

% AHQ[bc]	Relative Levels of Products as Compared to I.S. (1.0 area)		
	Dimer	Trimer	Adduct
0.0	3.5	8.5	--
2.5	1.4	1.3	0.2
5.0	1.3	0.9	0.5
10.0	1.2	0.7	0.2
20.0	1.1	0.4	0.7
40.0	1.1	0.2	0.8
100.0	1.0	0.2	0.7

[a] Two hours at 173°C, 30 mL of 0.5N NaOH, 154.0 ± 0.6 mg of vanillyl alcohol, titanium bombs, flushed with N_2 before sealing.

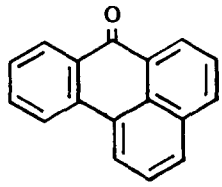
[b] Generated by adding the appropriate weight of AQ to the reaction mixture containing 540 mg of glucose. The percent is figured on a molarity basis (2.5% molarity basis = 3.3% on a weight basis).

[c] Comparing this percent to the percent used in pulping is difficult since (1) vanillyl alcohol has a lower molecular weight than the typical lignin monomer (138 to 172), (2) wood is only 25% lignin, (3) not all the lignin units in wood are capable of forming QM's, (4) most of the lignin units in wood that form QM's also further react by β-aryl ether cleavage and (5) vanillyl alcohol can only undergo condensation reactions.

One wonders if vanillyl alcohol can enter into redox reactions with AQ and AHQ. Two products which might be expected from a redox reaction of AQ and VA, are vanillin and vanillic acid. The former was observed in very small amounts in one of the GC/MS analyses. Extraction of the vanillyl alcohol cooked products

with carbonate produced no vanillic acid. In a personal communication, Gratzl (North Carolina State University) suggested that creseol (16) might be a redox reaction product. None of this was observed by GC in samples which were carefully worked up, trying to avoid the loss of volatile phenols.

Fleming and Fullerton have investigated AQ-black liquors from wood cooks and have found, by thin layer chromatography (TLC), several components which either fluoresce, like benzanthrone (20) or exhibit fluorescent quenching, like 2-vanillylanthraquinone (21) (79,80).



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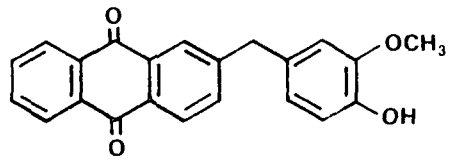

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Recently, Fleming has looked at the TLC behavior of two of our VA/AHQ cook samples and observed a spot, in small amount (<5% of the total), which appears to be 2-vanillylanthraquinone (21). The spot has the same R_f value and fluorescent quenching characteristic as 2-vanillylanthraquinone.

FUTURE RESEARCH AREAS

Even though we have learned a great deal about the reactions of vanillyl alcohol in alkali, there still remains the question of how AHQ prevents VA condensation reactions and what new reactions take over. The material discussed in the next section sheds some light on this problem; yet there are still a large number of

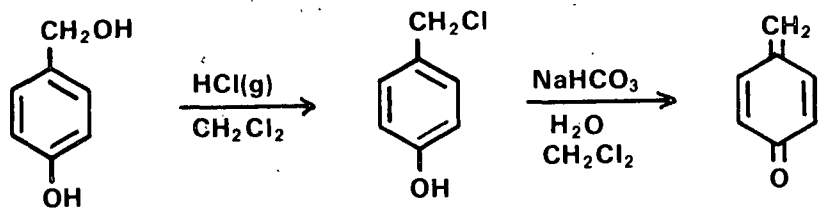
products unidentified in the VA/AHQ cooks. A ^{1}H-NMR of a VA/AHQ product mixture showed unexplained signals at 7.3-7.6 and 4.3 δ. The reaction mixtures will be re-examined when the Institute's new GC/MS arrives.

REACTIONS OF ANTHRAHYDROQUINONE WITH SIMPLE QUINONEMETHIDES

A question was raised earlier in this report: "How does AHQ react with QMs?" The simplest way to answer this question is to have AHQ present when a reaction known to generate QMs is in progress. Since QMs are quite reactive toward water and AQ is not very water soluble, it was thought that the best way to attack this problem was to use organic solvents as the reaction medium. Strong nucleophiles, which might react with QMs, would also be avoided.

PREPARATION OF QUINONEMETHIDES

Posisek, *et al.* have reported the UV spectrum of unsubstituted quinonemethide, generated in the following way (99):

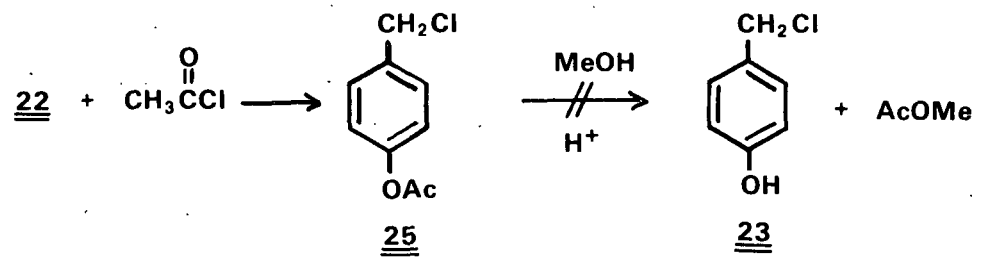


22 23 24 (2)

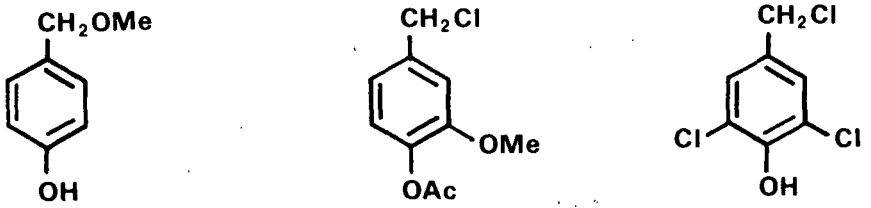
We tried several different procedures to repeat the reactions shown above but were unsuccessful in obtaining reasonable quantities of 23 or 24. Presumably, reactions like this can be done with HBr, using the proper techniques and rapid handling of the products (100).

An alternative method of preparing quinonemethide 24 was attempted, Eq. 3. Although the choloroacetate 25 could be easily prepared (101), its acidic cleavage (transesterification) gave only the ether 26. This latter step was followed by

NMR and there was no indication that 23 was even formed as an intermediate. Presumably, the QM 24 forms directly from 25 and rapidly reacts with methanol to give 26. A transamination reaction of 25 also was unsuccessful. The corresponding chloroacetate (27) from vanillyl alcohol was also prepared.

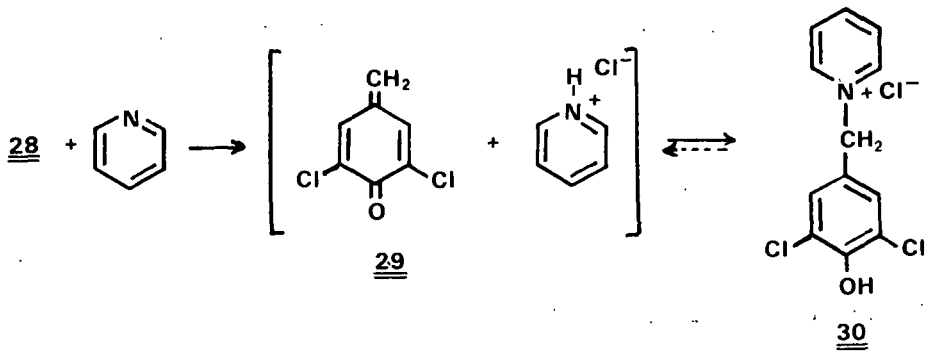


25 23 (3)



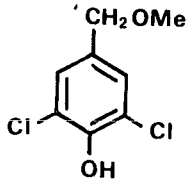
26 27 28

In a surprising reaction, 2,6-dichlorophenol could be chloromethylated to give a stable p-hydroxybenzyl chloride 28 (101). Several reactions were done with 28, but the most interesting one was its reaction with pyridine, Eq. (4).



29 30 (4)

The formation of the salt 30 probably occurs *via* a quinonemethide 29. The salt was recrystallized from water with gentle heating, but was unstable in refluxing methanol, providing ether 31 (probably *via* CH_3OH addition to 29). Consequently, Eq. (4) or its reverse looked to be a good way to generate a QM in the absence of a strong nucleophile and using organic solvents.



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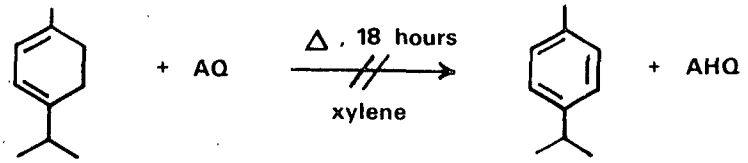
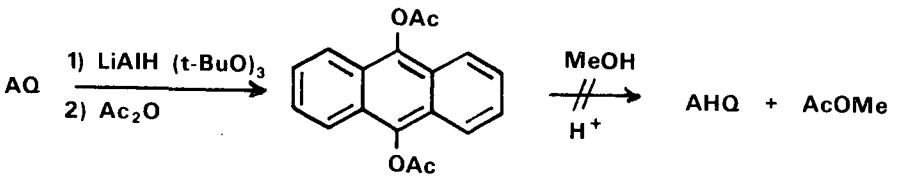
GENERATION OF PURE AHQ

Several methods were tried for generating dry AHQ. One was to disproportionate AQ with α-terpinene (32), Eq. (5); however only very poor yields of AHQ were observed. Another method was to reduce and acylate AQ to obtain AHQ diacetate 34 and then transesterify with methanol [Eq. (6)]. Surprisingly, AHQ diacetate is quite stable to acidic methanol, and AHQ could not be generated in this way.



(5)

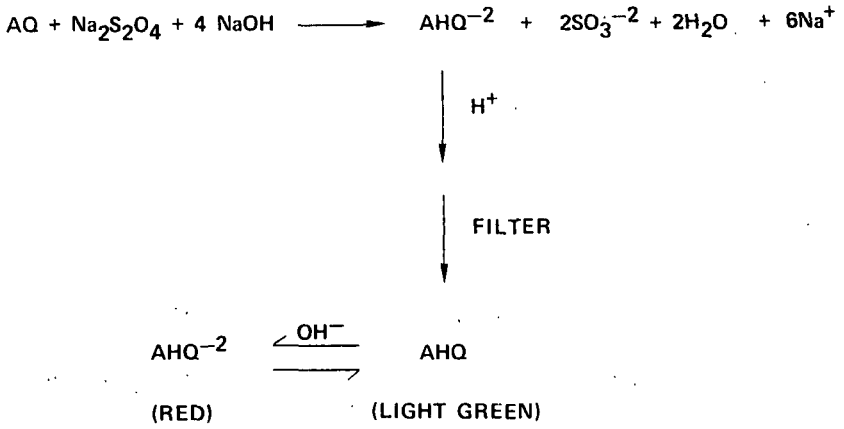
32 33



(6)

34

Two other methods for generating AHQ, which involve an aqueous solvent, are the reaction of AQ with glucose or sodium dithionite. The latter reaction is very simple to do and the progress of the reaction is easily followed by the color changes. This method was the principal one used in all our subsequent work. The reaction is outlined below; all steps were done under a nitrogen atmosphere. Dry AHQ could be obtained by gently heating the residue under vacuum to remove excess water.

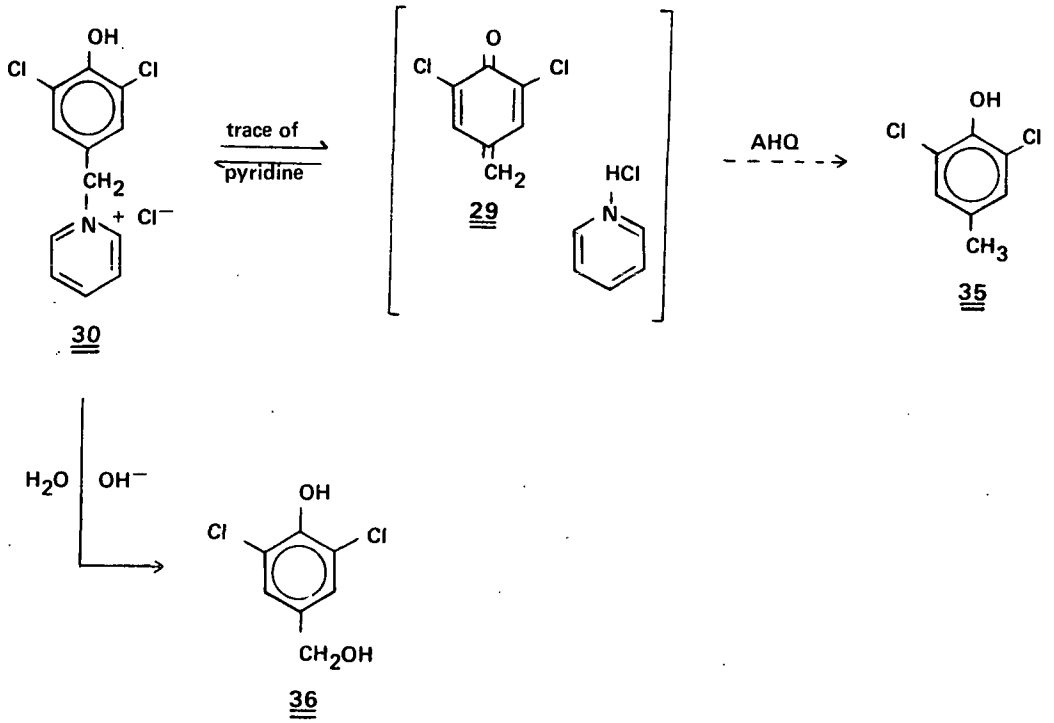


REACTIONS BETWEEN AHQ AND QM PRECURSORS

The pyridine salt 30 was mixed with anhydrous AHQ and a trace of pyridine in dioxane and heated for several hours. Work-up of the reaction provided recovered salt 30 and AQ (from AHQ and air). None of the hoped-for reduction product 35, which had been independently synthesized from p-cresol, could be detected [Eq. (7)].

The failure of AHQ to react might have been because of the form in which it was used. The light green anhydrous AHQ may be considerably less reactive than

the ionic, red colored AHQ which is present in aqueous base. This red colored species is either AHQ^{-2} (dianion), AHQ^{-1} (monoanion) or $AHQ^{\cdot}$ (radical anion or semiquinone),



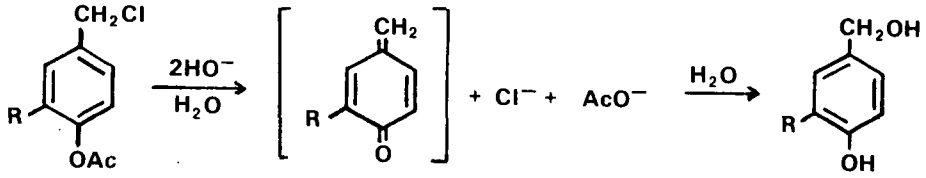
30 29 35 36

(7)

Interestingly, the salt 30, when added to aqueous basic AHQ, rapidly discharges the red color of the solution. A new product was also formed. This product was different from 3,5-dichloro-4-hydroxybenzyl alcohol (36), which could be produced by simply adding the pyridine salt to aqueous hydroxide. When subjected to gas chromatography, the product broke down, giving AQ and 36. The identity of this new product remained an unknown until the next set of experiments were performed.

The reaction of AHQ^{-2} with chloroacetates 25 and 27 was examined next. It was expected that these compounds would hydrolyze in aqueous base to give quinonemethides, which would quickly convert to p-hydroxybenzyl alcohol compounds

[Eq. (8)]. If, however, the reactions of the quinonemethides with AHQ dianion were fast, QM-AHQ products might be produced.



(8)

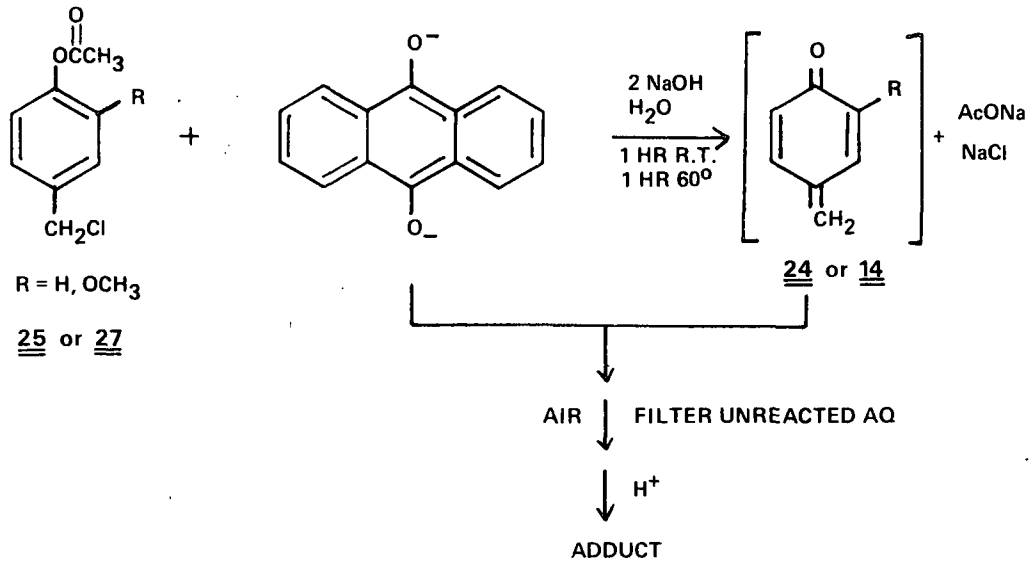
25 , R=H
27 , R=OMe

24 , R=H
14 , R=OMe

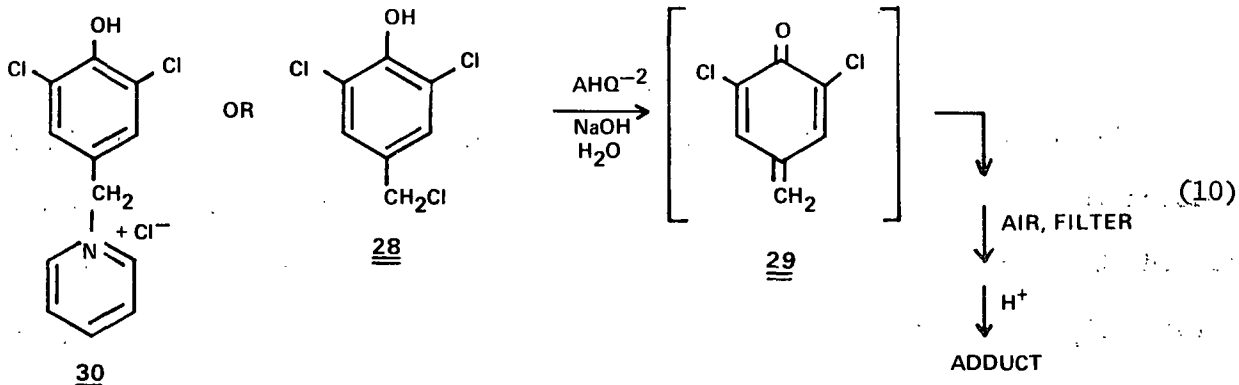
22 , R=H
12 , R=OMe

The dianion of AHQ was generated by the dithionite method. By appropriate manipulation of the pH and filtration, AHQ^{-2} was obtained free of the inorganic salts. [Actually, this purification was not necessary; the reactions proceeded just as well in the presence of the inorganic salts.] The AHQ^{-2} aqueous solution was made strongly alkaline and the chloroacetate was added. After stirring for 1 hr at room temperature and 1 hr at 60°C, the mixture was cooled to room temperature and exposed to air, allowing the excess AHQ to be converted to AQ. Filtration of the basic solution removed the AQ. Acidification of the filtrate gave a good yield of a solid, which proved to be a QM-AHQ adduct. The adduct was purified by recrystallization from methanol-water.

Three adducts, in yields of 70-98%, have been prepared by this procedure: one from 25, another from 27 and the third from either the chorophenol 28 or its pyridine salt 30, Eq. (9) and (10). The fact that they are one-to-one addition products of a QM and AHQ was established by elemental analysis and spectral means.


2 NaOH
H_2O
1 HR R.T.
1 HR 60°
AcONa
NaCl
R = H, OCH_3
25 or 27
24 or 14
AIR
FILTER UNREACTED AQ
H^+
ADDUCT

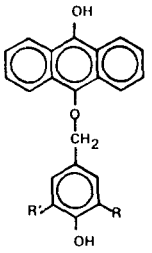
(9)


OR
AHQ^{-2}
NaOH
H_2O
28
29
30
AIR, FILTER
H^+
ADDUCT

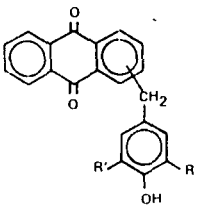
(10)

STRUCTURE PROOF OF THE QM-AHQ ADDUCTS

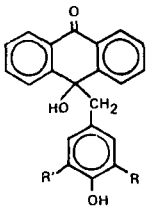
Reasonable candidates for the structures of the adducts are the following:



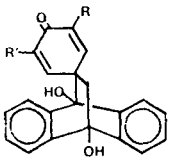
37



38



39



40

A) R=R'=H
B) R=R'=Cl
C) R=H, R'=OMe

All of these compounds would fit the elemental analysis data, Table II, and be reasonable from a mechanistic point of view. The charges on AHQ^{-2} can be delocalized, by resonance, between the oxygens and any of the carbons (Fig. 17). Structures 37, 38 and 39 can be thought of as arising from quinonemethide attack on an oxygen, side ring carbon and center ring carbon, respectively. Structure 40 could arise by a Diels-Alder type reaction (anthracene shows this type of chemistry) or an intramolecular cyclization of 41. Figure 17 considers ways in which 39 and 40 could form.

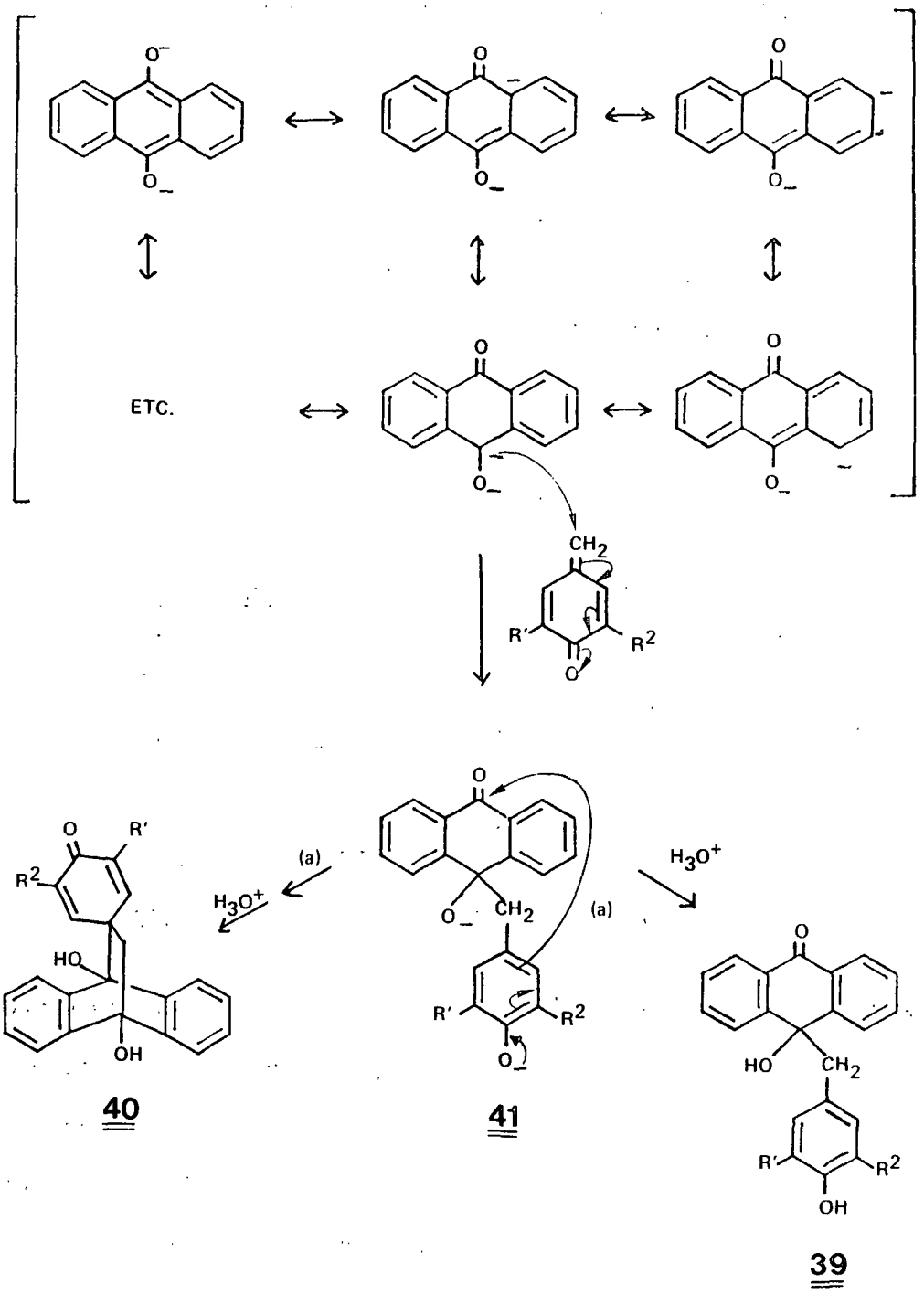
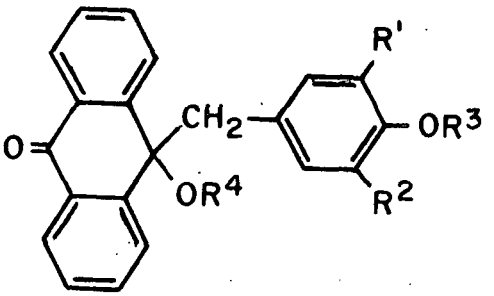


Figure 17. Mechanisms for the Formation of Possible QM-AHQ Adducts

TABLE II

ELEMENTAL ANALYSES OF QM-AHQ ADDUCTS AND DERIVATIVES



Compound				Calculated		Observed	
R^1	R^2	R^3	R^4	% C	% H	% C	% H
H	H	H	H	79.75	5.06	79.30	5.13
Cl	Cl	H	H	65.45	3.64	65.29	3.69
OMe	H	H	H	76.30	5.20	75.86	5.90
H	H	Ac	H	77.09	5.03	77.08	5.11
H	H	Ac	Ac	75.00	5.00	75.17	5.07

Structures 37 and 38 could be ruled out based on the following evidence. The infrared (IR) spectra of the adducts indicated the presence of both hydroxyl and carbonyl functional groups; the NMR evidence (to be considered in more detail shortly) established that the adducts had two hydroxyl groups and one carbonyl group. The simple adduct ($R = R^1 = H$) was treated with acetic anhydride under both mild and harsh conditions to give a mono and diacetate derivative, respectively. This latter piece of evidence indicates that the adduct has one hydroxyl group which is easy to acylate and one, probably because of a sterically hindered environment, which is difficult to acylate. Both structures 39 and 40 fit these criteria.

A detailed analysis of the ^{1}H and ^{13}C-NMR spectra of the adducts and the two acetate derivatives strongly indicated that the structure of the adducts was that of a 10-benzyl-10-hydroxyanthrone, 39. In fact, the alternative bicyclo[2.2.2]-octane structure 40 could be ruled out. The proton and carbon-13 NMR spectral data are given in Tables III and IV. The splitting patterns for the carbon signals were arrived at by running several off-resonance spectra. Appendix I shows the NMR spectra related to the unsubstituted QM-AHQ adduct 39A.

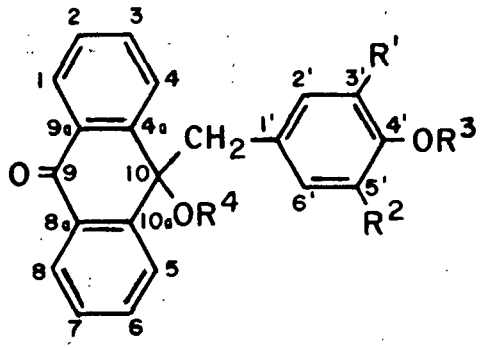
The adduct spectra were run in DMSO-d_6 as the solvent. The hydroxyl proton resonances in DMSO are known to have very specific locations depending upon type: aliphatic OH is 4.0-4.5, benzyl OH is 5.2 and phenolic OH is 9.2 δ (102). The adducts show hydroxyls at 8.5-9.7 (phenolic) and 6.4-6.5 (dibenzyl), both of which can be washed away by the addition of D_2O to the solutions. Structure 40 has only benzylic type hydroxyls.

The calculated chemical shifts (peak locations) for the $-CH_2-$ group in structures 39 and 40 are 3.40 and 2.70 δ, respectively; the observed is 3.07, midway between the two calculations. [These calculations, where multiple groups are present, are generally too high, rather than too low.] The ^{13}C-NMR spectra show only 2 aliphatic signals, i.e., chemical shifts below 100 ppm; this is compatible with structure 39 but not structure 40, which has four aliphatic carbons.

The assignment of the signals in the ^{13}C-NMR spectra was based on a comparison to the published spectra of anthraquinone (103-105) and anthrone 42 (103,106) and the observed shifts which occurred upon acylation of the C-10 hydroxyl groups. A change at C-10 should affect the benzyl carbon and carbons 4, 4a, 10, 10a and 5 more than the other carbons (the numbering is given in Table 3). On comparing the spectra of the adducts to that of anthrone, we assume C-10 and C-4a,

TABLE III

^{1}H-NMR SPECTRAL ASSIGNMENT FOR THE QM-AHQ ADDUCTS[a,b]



Solvent	DMSO	DMSO	DMSO	$CDCl_3$	$CDCl_3$	$CDCl_3$
R^1	H	Cl	OCH_3		H	H
R^2	H	Cl	H		H	H
R^3	H	H	H		Ac	Ac
R^4	H	H	H		H	Ac
Phenolic OH	9.00_1^s	9.70_1^s	8.54_1^s	5.44_1^s		
Aliphatic OH	6.40_1^s	6.52_1^s	6.46_1^s	2.98_1^s	3.00_1^s	
C_1-C_8 protons	$7.4\text{-}8.1_8^m$	$7.4\text{-}8.1_8^m$	$7.4\text{-}8.1_8^m$	$7.2\text{-}7.9_8^m$	$7.2\text{-}8.1_8^m$	$7.2\text{-}7.6_6^m$, $8.12_2^{d,J=8Hz}$
C_2' proton	$6.16_2^{d,J=9Hz}$	5.90_2^s	5.32_1^m	$5.42_1^{d,J=1Hz}$	$6.58_2^{d,J=9Hz}$	$6.63_2^{d,J=9Hz}$
C_6' proton			$6.18_1^{d,J=9Hz}$	$6.40_1^{d,J=9Hz}$		
C_3' proton	$5.68_2^{d,J=9Hz}$				$6.13_2^{d,J=9Hz}$	$6.15_2^{d,J=9Hz}$
C_5' proton			5.32_1^m	$5.66_1^{d\ of\ d}$		
$-CH_2-$	3.06_2^s	3.08_2^s	3.08_2^s	3.09	3.12_2^s	3.34_2^s
Other			3.20_3^s	3.34_3^s	2.16_3^s	2.16_3^s, 2.19_3^s

[a] Superscript on the assignments refers to splitting pattern, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; the subscript on the assignments refers to relative integrated area of the signal; the J value refers to the coupling constant.

[b] All signals are reported in PPM (δ) units, relative to TMS.

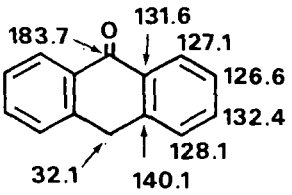
TABLE IV

^{13}C-NMR SPECTRAL ASSIGNMENT FOR THE QM-AHQ ADDUCTS[a]

Solvent	DMSO	DMSO	DMSO	$CDCl_3$	$CDCl_3$
R^1	H	Cl	OCH_3	H	H
R^2	H	Cl	H	H	H
R^3	H	H	H	Ac	Ac
R^4	H	H	H	H	Ac
C_1, C_8	127.7^{d}_{ℓ}	128.0^{d}_{ℓ}	128.0^{d}_{ℓ}	128.4^{d}_{ℓ}	127.7^{d}_{ℓ}
C_2, C_7	126.8^{d}_{ℓ}	127.0^{d}_{ℓ}	127.2^{d}_{ℓ}	127.0^{d}_{ℓ}	126.8^{d}_{ℓ}
C_3, C_6	133.6^{d}_{ℓ}	133.6^{d}_{ℓ}	133.8^{d}_{ℓ}	133.4^{d}_{ℓ}	133.1^{d}_{ℓ}
C_4, C_5	125.3^{d}_{ℓ}	125.6^{d}_{ℓ}	125.2^{d}_{ℓ}	126.2^{d}_{ℓ}	123.8^{d}_{ℓ}
C_{8a}, C_{9a}	130.8^{s}	131.1^{s}_{m}	131.4^{s}_{w-m}	132.6^{s}_{w}	130.7^{s}_{w}
C_{4a}, C_{10a}	148.0^{s}_{m}	(147.8^{s}_{m})	148.3^{s}_{m}	147.2^{s}_{w}	143.4^{s}_{w}
C_9	182.4^{s}_{w}	182.6^{s}_{w}	183.0^{s}_{w}	183.4^{s}_{w}	181.8^{s}_{w}
C_{10}	73.0^{s}_{m}	72.6^{s}_{m}	73.2^{s}_{m}	73.8^{s}_{w}	79.0^{s}_{w}
$-CH_2-$	54.8^{t}_{w-m}	53.9^{t}_{m}	55.3^{t}_{m}	54.8^{t}_{m}	52.7^{t}_{m}
C_1'	125.1^{s}_{m}	128.4^{s}_{m}	125.4^{s}_{m}	131.3^{s}_{w}	130.2^{s}_{w}
C_2' C_6'	130.8^{d}_{ℓ}	130.2^{d}_{ℓ}	114.2^{d}_{m} 122.8^{d}_{m}	131.4^{d}_{ℓ}	131.7^{d}_{ℓ}
C_3' C_5'	114.2^{d}_{ℓ}	121.2^{s}_{m}	147.0^{s}_{w-m} 114.6^{d}	120.6^{d}_{ℓ}	120.3^{d}_{ℓ}
C_4'	156.0^{s}_{w-m}	(147.8^{s}_{m})	145.2^{s}_{w-m}	151.0^{s}_{w}	149.4^{s}_{w}
Ester $\diagdown$C=O	--	--	--	169.8^{s}_{w}	168.7^{s}_{w}, 168.0^{s}_{w}
OH_3	--	--	--	21.0^{q}_{w-m}	21.6^{q}_{m}, 21.0^{q}_{m}

[a] Refer to Table III for the nomenclature and meaning of superscripts; the subscripts in this table refer to intensity of the signal; w = weak, m = moderate and ℓ = large.

10a are shifted downfield due to the attached substituents on C-10 and that C-4,5 are shifted upfield due to steric compression. The phenolic ring assignments agree quite well with phenol models 43, (107) 44, 45, 46, (108) and 47 (calculated from 43 and known (109) acetate shifts). The methoxyl substituted adduct 39C is also shown below for comparison purposes.



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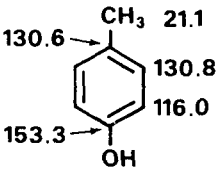

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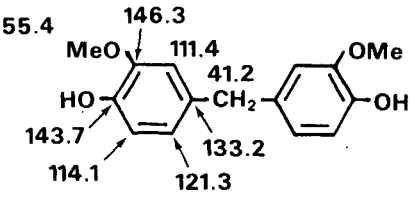

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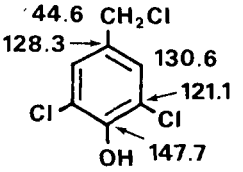

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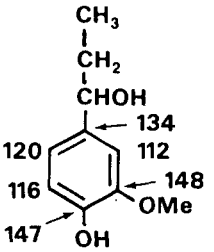

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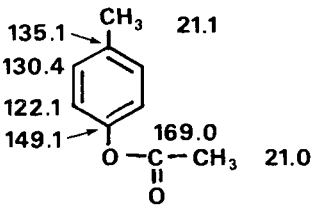

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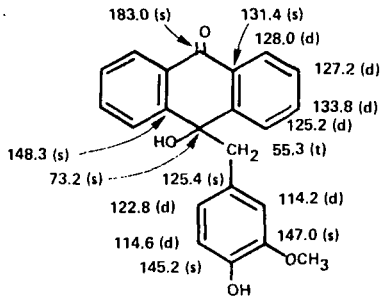


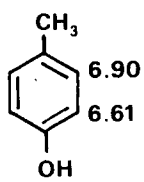
39C

The proton NMR spectrum of the diacetate derivative was quite informative. The C-1, C-8 protons were shifted far enough downfield to be seen as a doublet; the other 6 anthrone protons have the expected chemical shifts. Two types of acetate methyl signals, indicative of an aliphatic and aromatic acetate, were observed. The benzyl protons were seen downfield, probably because of the closeness to the

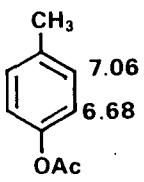
C-10 acetoxy group. The IR spectra of diacetate also shows both aliphatic and aromatic acetates.

Mass spectra were also obtained *via* GC/MS for methylated derivatives of QM-AHQ adducts 39A (unsubstituted) and 39C (methoxy substituted); the tabulated spectra are given in Appendix II. The spectrum of the diacetate of 39A was also obtained by GC/MS. Peak intensities are not always valid by this technique; however, the spectra were in good agreement with the proposed structures, displaying the anticipated molecular ions and reasonable fragmentation patterns.

The evidence discussed so far is very convincing for the adducts' structures to be of the type indicated by 39. What has not been discussed yet is the position of the phenolic proton signals in the ^{1}H-NMR spectra. The signals are considerably further upfield than would have been predicted based on structure 39. For example, the proton spectra of phenols generally shows signals in the 6.6-7.0 for the aryl hydrogens; the adducts' corresponding signals are at 5.3-6.6. Some model compound examples are given below.



43



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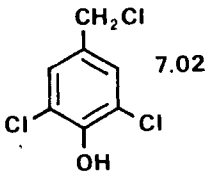

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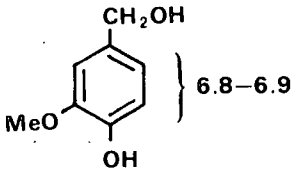
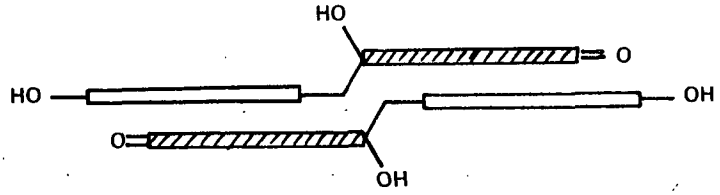


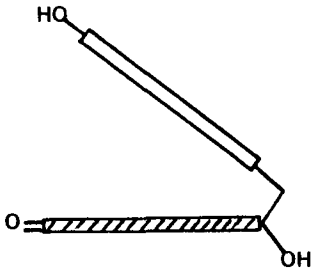
12

The upfield shifts can be explained by assuming the QM-AHQ adducts exist as either dimers (49) or sandwich structures (50), such that the phenolic ring hydrogens are situated in a magnetically shielded region near the anthrone ring system. In structures 49 and 50 the anthrone ring system is shaded. Stacking of

π-electrons from one aromatic to another, especially where one ring is electron rich (phenol) and the other electron poor (aryl ketone), is quite common (110). If the interaction is strong enough, charge transfer complexes can be formed.

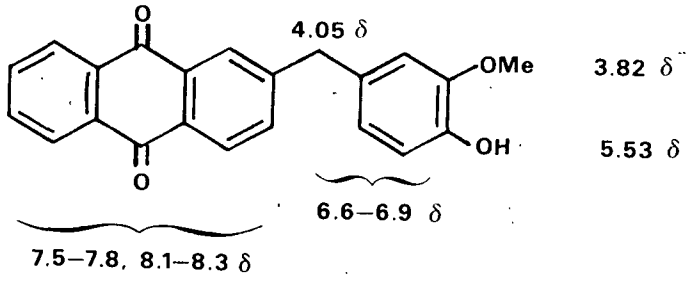


49



50

It is interesting to note that the ^{1}H-NMR of 2-vanillylanthraquinone shows no evidence of π-π sandwiching of rings. Molecular models show that the sandwiching phenomenon can only occur when the benzyl substituent is located on the 10-position of an anthrone skeleton. The NMR values for 2-vanillyl anthraquinone are given below (80).



Ultraviolet spectra were recorded for the QM-AHQ adducts in hopes of observing charge transfer bands. The general rule which has been applied as a criteria for the existence of charge transfer complexes between two species is

that the complex will exhibit UV absorption bands not present in the spectra of the individual pure components (110). For the QM-AHQ adducts, one would expect the UV spectra to be the sum of the individual contributions of a phenol unit and an anthrone unit, if there were no charge transfer interactions. Phenols and quinones are known to exhibit charge transfer complexes (110). Phenols absorb in the 270-280 nm region, but the intensity is somewhat weak ($\varepsilon \simeq 1{,}500$) (111,112). Anthrone shows a strong (ε 25,000) absorption at 257 nm, which gradually tails off at higher wavelength (113).

The UV spectra of the QM-AHQ adducts 39, R = R' = H, R = R' = Cl and R = H, R' = OCH_3, displayed $\lambda_{max}^{ethanol}$ at 277 (ε 12,000), 278 (ε 12,000) and 272 nm (ε 13,000), respectively. This data, together with the NMR evidence, supports the picture that the phenol and anthrone subunits exhibit some π-π sandwiching in the QM-AHQ adducts. Although the data do not allow a distinction to be made between the dimer structure 49 or folded-over structure 50, we prefer the latter. Molecular models indicate the benzyl methylene interferes with good stacking (for the dimer structure); this is especially apparent for substituted benzyl carbon adducts, which we have prepared and still see the peculiar NMR shifts characteristic of the π-π interaction of aromatic rings.

REACTIONS BETWEEN AHQ AND *p*-HYDROXYBENZYL ALCOHOLS

In an earlier section we established that AHQ retards the condensation reactions of vanillyl alcohol. Since vanillyl alcohol is capable of forming quinonemethides in alkaline media, the retardation of condensation reactions may be a result of a preferential reaction of the QM with AHQ to give an adduct, namely 39C.

The gas chromatogram of the derivatized product mixture from the reaction of vanillyl alcohol with alkali at 173° in the presence of AHQ displayed a small signal, retention time slightly longer than the dimer products, which corresponded exactly in GC/MS to the methylated derivative of adduct 39C (Fig. 18). This adduct component only appeared in the AHQ cooks (Fig. 14). Its low yield (ca. <1%) can be attributed to its instability at 173°; nearly all of a pure sample of adduct 39C decomposed when heated at 173° in alkali for 2 hr.

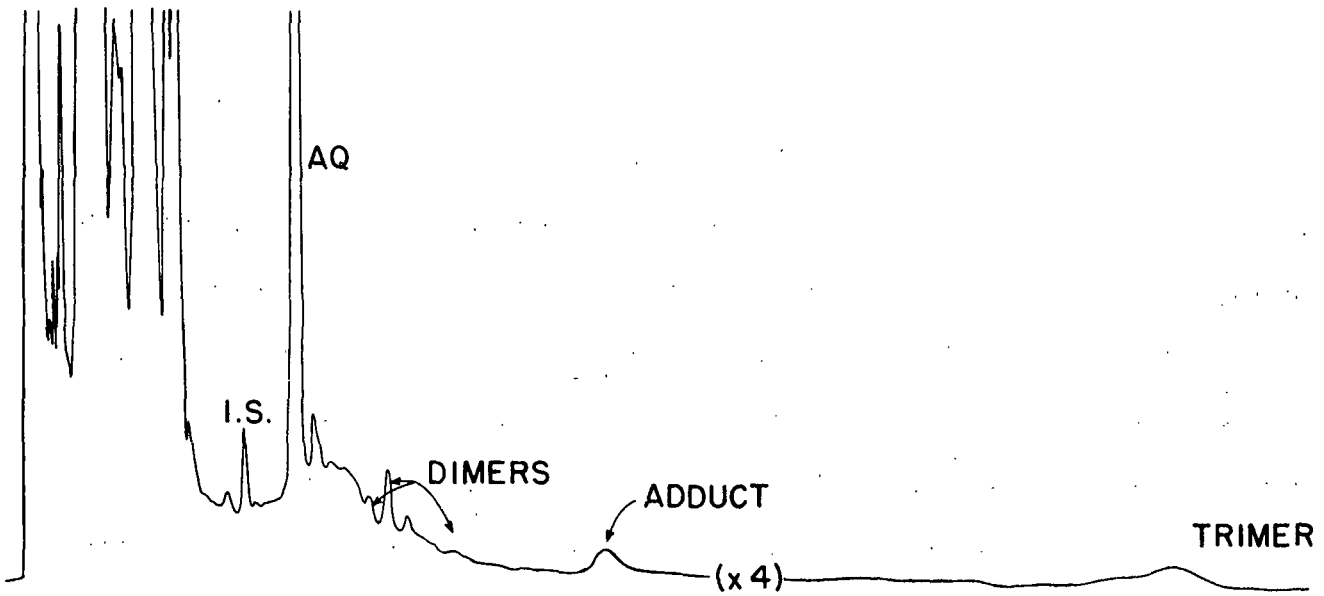


Figure 18. Gas Chromatograph of the Methylated Product Mixture from the Reaction of Vanillyl Alcohol with Alkali in the Presence of AQ and Glucose

The yield of adduct increased somewhat (ca. ≃ 2%) when vanillyl alcohol was heated at 60° for 1 hr with AHQ (generated by the dithionite method). Also produced in this reaction were substantial levels of condensation materials, particularly dimer 19 — a minor component in the 173° cook products. The yield of adduct 39C from reaction of AHQ with the chloroacetate 27, under the same conditions as above, was 80%. If condensation products occurred in the chloroacetate reaction,

their presence was not enough to interfere with purification of the resulting adduct. Figure 19 shows the production of adduct 39C from the two precursors discussed.

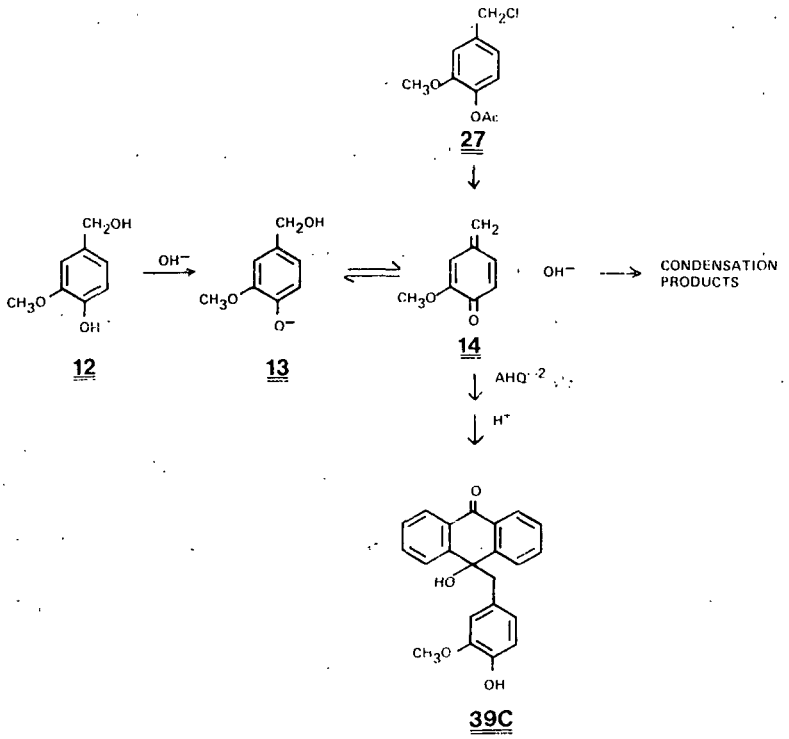


Figure 19. Production of Adduct 39C from Two Precursors

Why should the yield of adduct be so low and level of condensation products be so high in the vanillyl alcohol reactions done at 60°? Very few condensation products were observed when vanillyl alcohol was heated at 173° in the presence of AHQ. A possible explanation may be related to the levels of phenolate (13) and quinonemethide (14) produced under these different conditions. High temperatures should favor production of the relatively unstable QM from the phenolate. In other words, the equilibrium phenolate 13 $\rightleftharpoons$ QM 14 should shift to the right at high temperatures. The following rate expressions can be set up:

$$\text{Rate}_{\text{condensation}} = k_{\text{cond.}}\,[\text{phenolate}][\text{QM}]$$

$$\text{Rate}_{\text{adduct formation}} = k_{\text{ad.}}\,[\text{AHQ}^{-2}][\text{QM}]$$

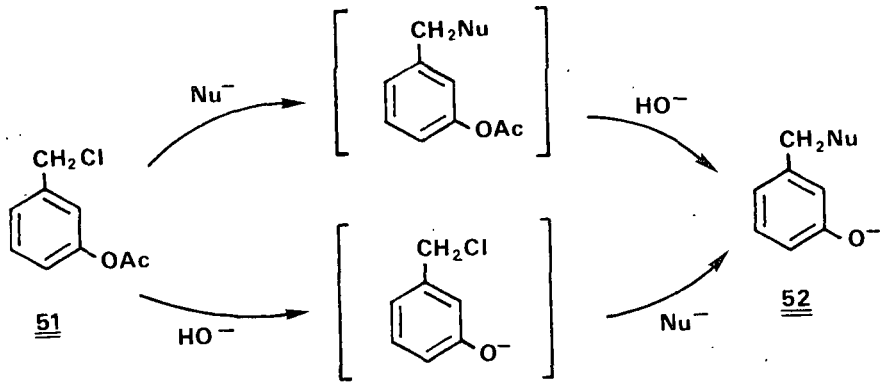
At high temperatures [QM] increases and [phenolate] decreases, thus favoring adduct formation. When the chloroacetate is used to generate the QM, there is no phenolate present initially; therefore, condensation reactions should be low.

Another explanation of the differences in the levels of condensation products at 60° *vs.* 173° is that adduct formation reactions may respond more to increases in temperature than do condensation reactions.

p-Hydroxybenzyl alcohol 22 has also been used as a substrate in 60° reactions with AHQ and alkali. The results were similar to those just discussed for its methoxy substituted analog, vanillyl alcohol. A low, but real, yield of adduct 39A was observed, along with numerous condensation products.

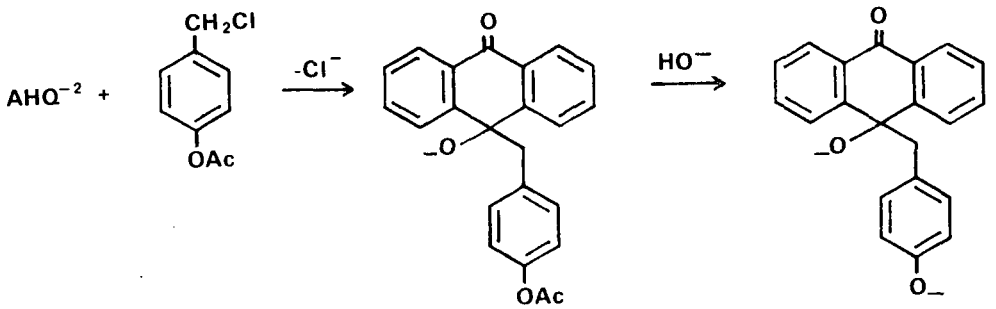
ARE QMs INVOLVED?

So far we have assumed that the adducts form by reaction of a quinonemethide with AHQ^{-2}. The assumption is based on Taylor's report (101) that *p*-acetoxybenzyl chloride 25 reacts with heteroatom nucleophiles *via* a quinonemethide; this conclusion was arrived at by comparing reactivity differences of the *para* compound to the *meta* isomer 51. The latter can only react with nucleophiles *via* S_N2 mechanism [Eq. (11)].



(11)

Since chloride is a good leaving group, the following mechanism should be considered as an alternative to the quinonemethide mechanism for the formation of adducts:



(12)

A displacement mechanism, like the one shown above, is much less likely with a *p*-hydroxybenzyl alcohol since OH is a poor leaving group. This fact could explain the low yield of adducts when *p*-hydroxybenzyl alcohols were used as a substrate.

In order to better understand the mechanism for the production of the QM-AHQ adducts, we decided to see how the *meta*-acetoxy chloride 51 behaved as a substrate. Unfortunately, this compound proved to be extremely difficult to prepare in a pure form. Taylor, in a personal communication, indicated that their group also experienced some problems preparing 51.

Another approach taken was to prepare 54 and react it with AHQ^{-2}; some adduct was formed in this reaction (Fig. 20). The only reasonable way that adduct 39A can be produced is *via* a quinonemethide, since there is no good leaving group for a displacement mechanism. [The fact that quinonemethides can be liberated from anthrone skeletons will be further developed in a later section of this report.]

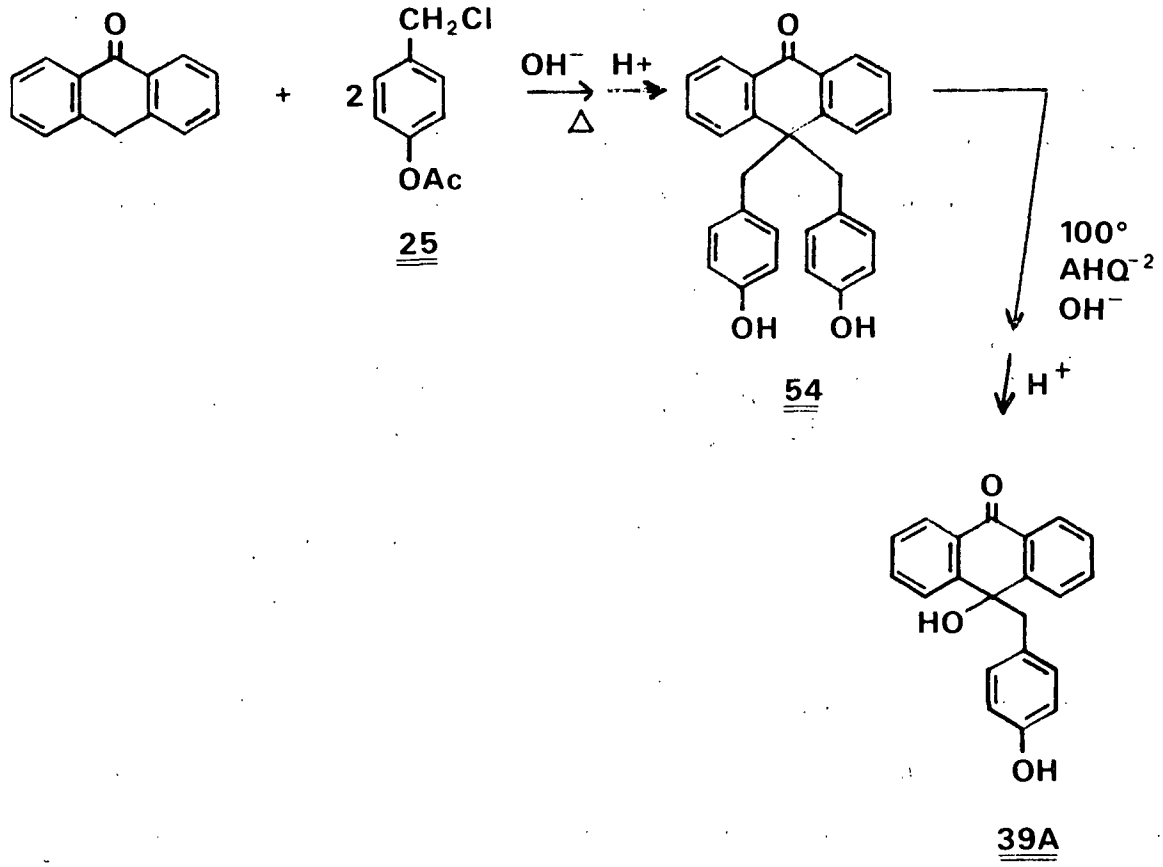


Figure 20. Production on an Adduct *via* a Quinonemethide Intermediate

Supporting evidence for the production of QM-AHQ adducts from QMs comes from the recent work of Landucii (74). He has treated a lignin model compound 55 with HBr to presumably give 56, which was not isolated but treated with aqueous carbonate to give a QM 57 (Fig. 21). The QM was extracted from the aqueous solution,

as it formed, with methylene chloride. Landucci has recorded UV spectra on the methylene chloride solution and has evidence for a QM in solution which is fairly rapidly lost upon standing at room temperature. Reaction of the methylene chloride solution with AHQ^{-2} produced the adduct 58 in good yield.

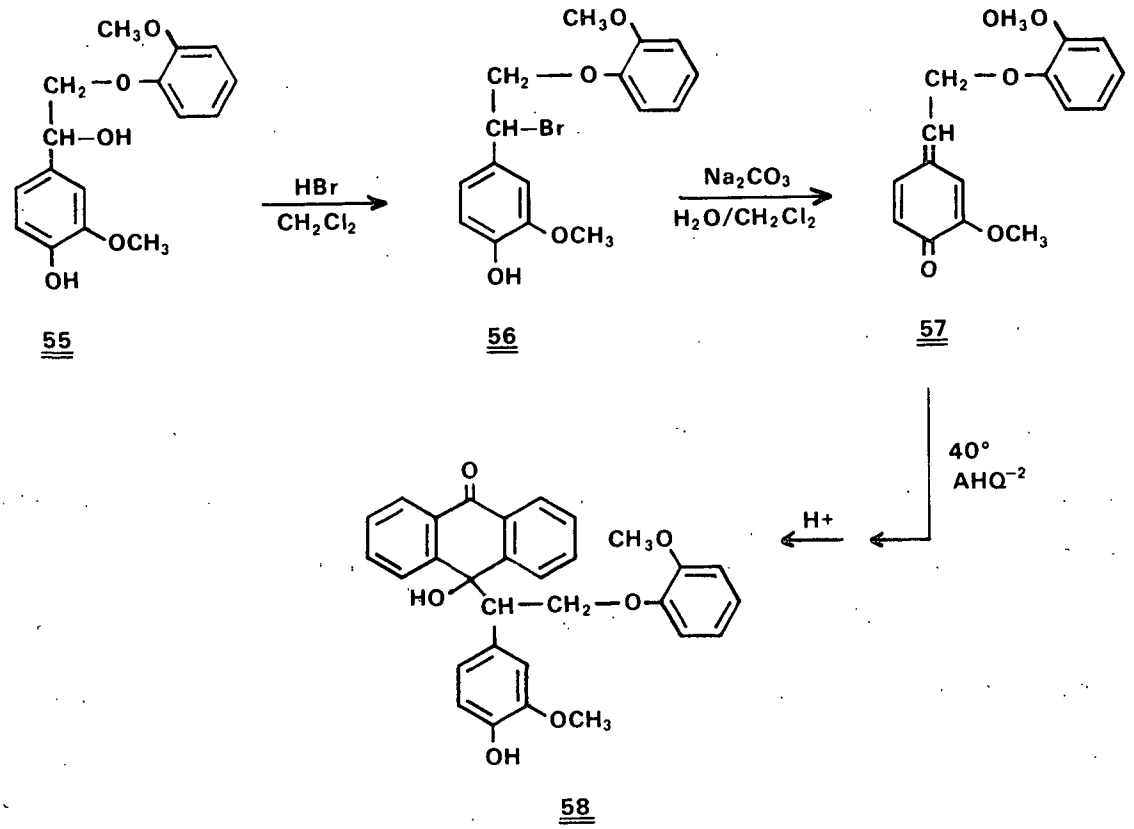


Figure 21. Landucci's (74) Procedure for Producing QM-AHQ Adducts

OTHER REACTIONS OF ANTHRAHYDROQUINONE

The possibility that O-alkylated QM-AHQ adducts may be intermediates in AQ pulping reactions prompted much of the following work. The motivation for the work was largely a response to an unpublished claim by Gierer of the preparation of an O-alkylated QM-AHQ adduct. This was in conflict with our findings. Landucci's (74) revision of Gierer's claim came to our attention after most of our work was complete. Essentially, Landucci's and our work nicely complement one another. Gierer has since published his study on fragmentation reactions of a lignin model *via* a QM-AHQ adduct, incorporating a C-alkylated intermediate (73).

VARIATION IN REACTION CONDITIONS

p-Acetoxybenzyl chloride 25 was mixed with AHQ^{-2}, base and 1:1 aqueous dioxane for 4-hr at 40° (Gierer's conditions) and worked-up to give the same anthrone adduct (39A) as isolated before. In a second experiment, the chloroacetate was added to the AHQ^{-2}/OH^{-}/1:1 aqueous-dioxane solution and the reaction terminated one min later when the color of the solution changed from red to a dark green. A 90% yield of anthrone adduct 39A was isolated. Apparently, time, temperature and solvent polarity have little influence on the course of the reaction; the product was always a C-alkylated one. If an O-alkylated intermediate 59 had formed first, as shown in Fig. 22, it would have to completely rearrange to a C-alkylated product in one min.

VARIATION IN SUBSTRATES

Deshpande reported in 1978 that AHQ^{-2} reacts with allyl bromide to give a C-alkylated product 60 (114). Very recently, Fullerton and Ahern (79) have reported that 10 can be obtained from the reaction of coniferyl alcohol 61 with AQ/glucose;

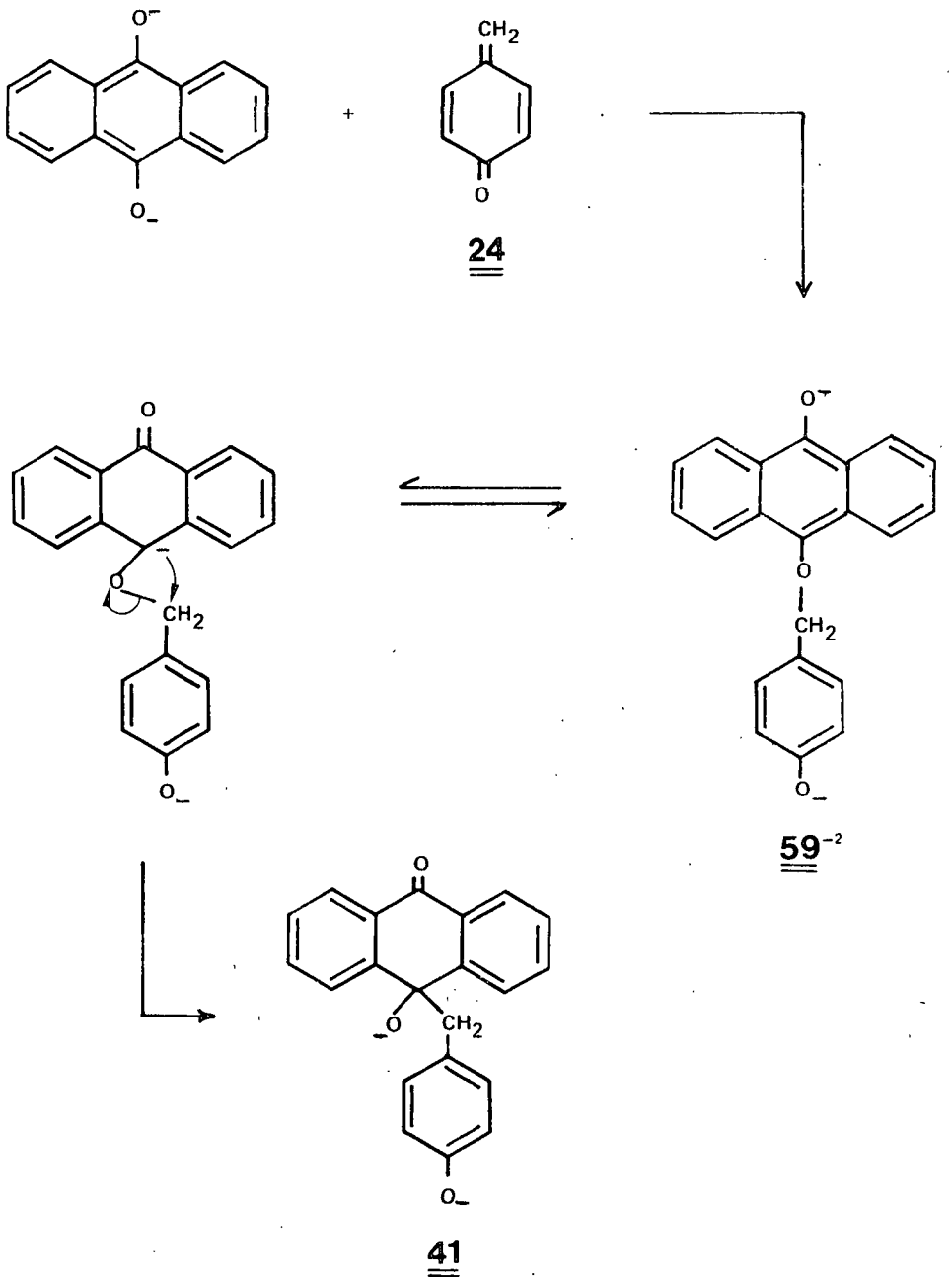
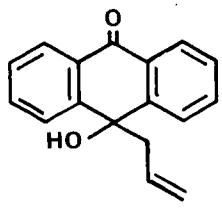
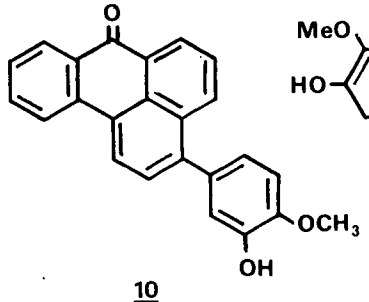


Figure 22. Production of a C-alkylated QM-AHQ Adduct from an O-alkylated Adduct

presumably, the C-alkylated derivative 62 is an intermediate in this reaction. We have alkylated AHQ^{-2} with benzyl chloride and obtained a 60% yield of C-alkylated product 63.



60



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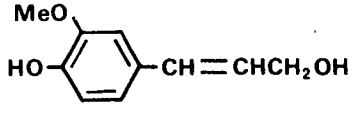

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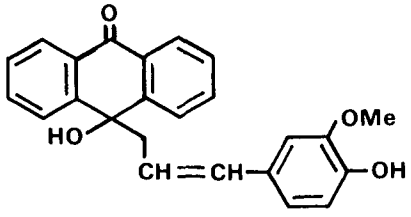

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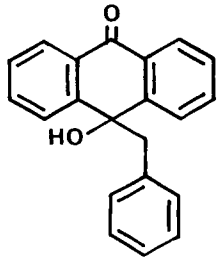
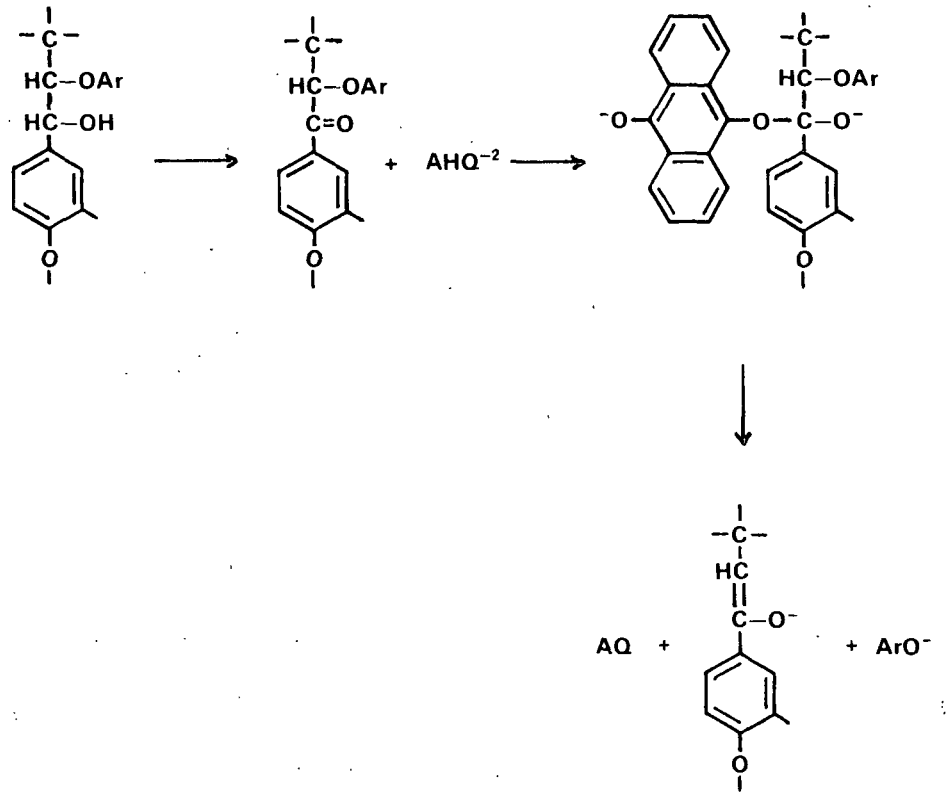


63

The ^{1}H-NMR of 63 showed the same upfield shifts for the aromatic signals noted for the QM-AHQ adducts (see Appendix II for details). Deshpande (114) notes that the allyl derivative 60 displays upfield vinyl signals in the 4.2-5.2 δ region. A dimethyl allyl derivative is reported to have methyl signals at 0.79 and 1.34, instead of the expected 1.8 δ region (114). Obviously, these compounds exist in sandwich conformations, as explained earlier.

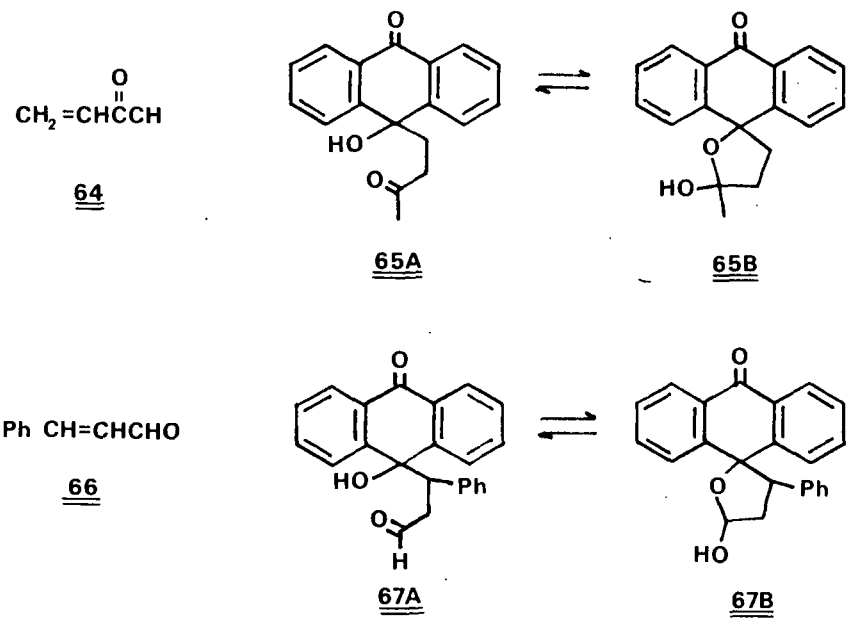
In the pulping of wood a great variety of different organic compounds can be generated, i.e., aromatic ketones and cinnamaldehyde structures from lignin, aliphatic ketones from carbohydrates, etc. Gratzl and coworkers have proposed

(92,93) that AQ is capable of oxidizing lignin to α-keto structures and that the latter can fragment *via* an O-alkylated AHQ adduct species [Eq. (13)].



(13)

It seemed important to establish what kind of substrates could interact with AHQ^{-2}. We have already shown that quinonemethides derived from reactive precursors or *p*-hydroxybenzyl alcohols, are suitable substrates. Benzyl chloride, allyl bromide (114) and coniferyl alcohol (75) also react with AHQ^{-2}. We have now expanded this list to include α,β-unsaturated carbonyl compounds, represented by methyl vinyl ketone (64), which gave adduct 65 in 54% yield, and cinnamaldehyde (66), which gave adduct 67 in about 40% yield.

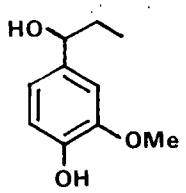


The adducts 65 and 67 were characterized by elemental analysis, IR, ^{1}H- and ^{13}C-NMR spectroscopy; see Appendix II for details. Based on the spectral evidence, adduct 65 exists in the open structure (65A), while the cinnamaldehyde adduct prefers the closed structure (67B).

No trace of adducts were observed when AHQ^{-2} was reacted with either acetone (CH_3COCH_3), benzaldehyde (PhCHO) or acetovanillone (4-OH-3-OMe-$PhCOCH_3$). This suggests that intermediate adducts like that shown in Eq. (13) have no real stability, if any existence at all.

The chloroacetate 69 was prepared from 68 and then reacted with AHQ^{-2} at 60° to give adduct 70 in about 25% isolated yield. The purpose of this set of reactions was to show that adducts can be produced even when the benzyl carbon is substituted. With substituted QMs, as is the case for QMs derived from lignin,

a known reaction is that of the base induced conversion of the QM (71) to a styrenyl structure (72). Obviously adduct formation can compete successfully with this kind of reaction. Landucci's results (74) also agree with this conclusion.



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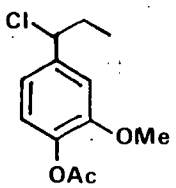

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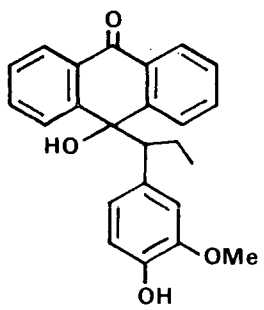

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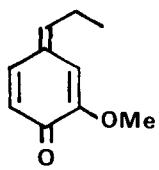

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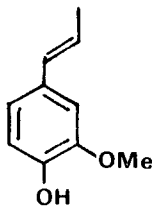

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CONCLUSIONS

There is no evidence to date that AHQ^{-2} can be alkylated at oxygen to give a stable product. With bulky QMs, such as 71, there was not even a hint in the NMR spectrum of the crude reaction product of 69 with AHQ^{-2} that any O-alkylated products had been produced. Considering bond and resonance energies, we estimate that a C-10 substituted adduct (like 70) should be about 23 kcal more stable than an O-alkylated product; roughly, C-alklylation should occur 10^{16} times more often than O-alkylation at room temperature.

Alkylation of AHQ^{-2} at one of the two side rings should have a higher activation energy than alkylation at C-10 since some aromaticity must be lost during the process. However, if the alkylation reactions are reversible, side ring alkylation should increase since the products of this alkylation appear to be more stable than C-10 alkylated products. This fact may account for the appearance of 2-vanillylanthraqinone (a C-2 alkylated product) in black liquors (80) and in our vanillyl alcohol cooks done at 173°C.

CHEMISTRY OF QM-AHQ ADDUCTS

The adducts that we and others have prepared from simple lignin models probably have parallels in actual pulping chemistry. An understanding of the chemistry of the adducts may help explain the effects of anthraquinone in pulping systems.

ALKALI REACTIONS AT 60-90° IN AIR

Each of the three adducts (39A-C) prepared from AHQ^{-2} and quinonemethide precursors, as described earlier, were placed in aqueous alkali and warmed to 60° (the temperature which was used to prepare the adducts). The dichloroadduct (39B) was recovered "unchanged" after acidic work-up. The low reactivity of this adduct may be due to an extremely low solubility in aqueous alkali.

The unsubstituted adduct 39A was first warmed in a nitrogen atmosphere and the yellow solution became red in color. When the pure nitrogen atmosphere was removed and the solution exposed to the air, the color became orangish. After about 20 min the color returned to a light yellow color and the solution contained a large amount of insoluble material. Filtration of this solution, while still basic, produced a solid (AQ) and a filtrate. Acidification of the filtrate, followed by ether extraction afforded a small amount of solid and a liquid residue. Analysis of the liquid by GC and NMR showed it to be a mixture of condensation products. Because of the presence of impurities and the small amount available, the solid product was not characterized at the time. Heating *p*-hydroxybenzyl alcohol with alkali at 60° gave similar condensation products; however, the materials were not characterized.

The methoxy adduct 39C was treated in the same way and gave results similar to the unsubstituted adduct. However, in this case the condensation products were identical to those which had already been characterized from the vanillyl alcohol cooks. The observed color changes, together with the production of AQ and condensation products, can be best understood by the reactions shown in Fig. 23.

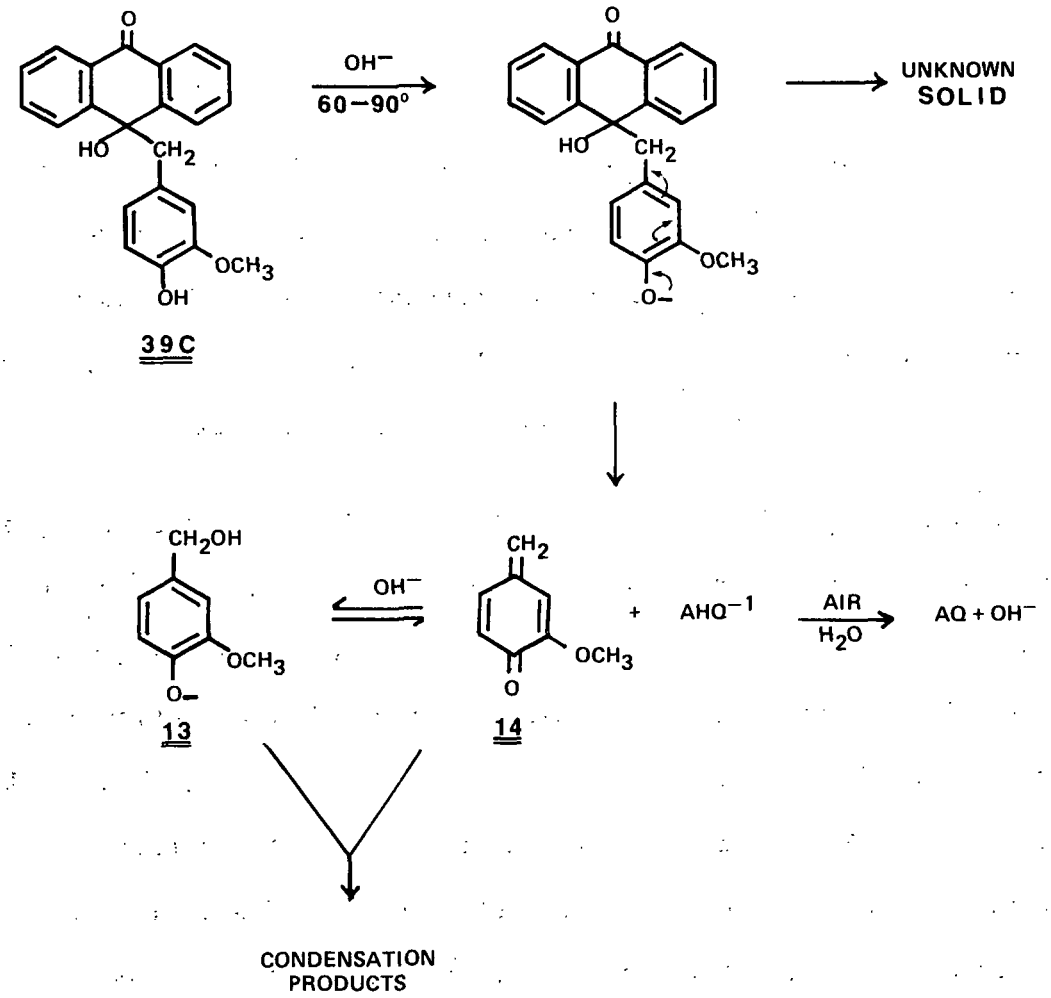
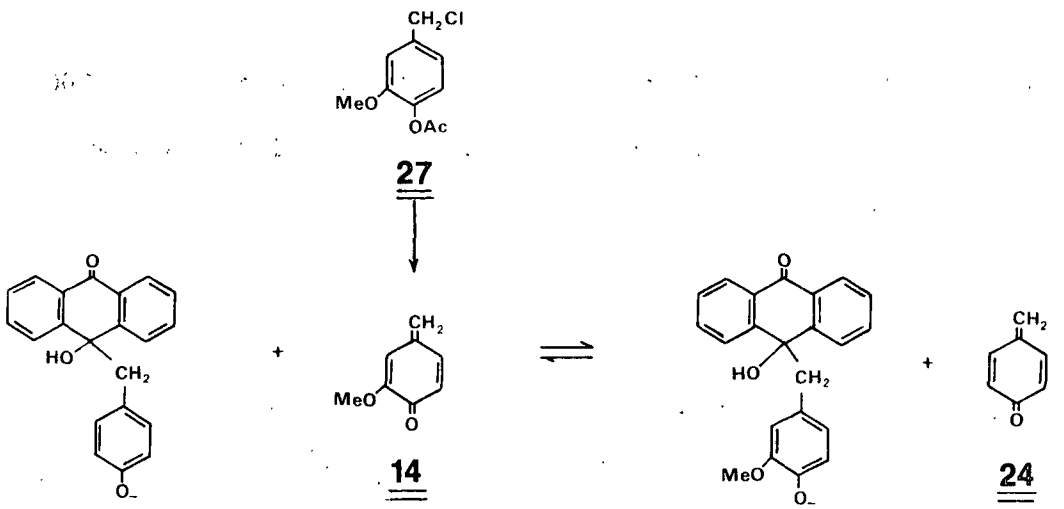


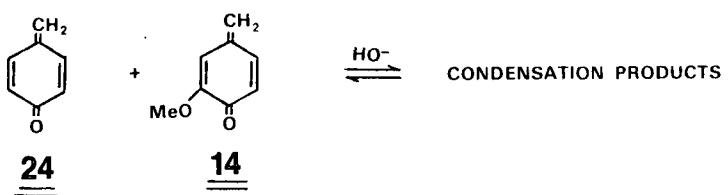
Figure 23. Reaction of QM-AHQ Adduct 39C with Alkali at 60-90°

We know that adducts can be formed from AHQ and QMs at 60°; these latest results show that the reaction is reversible — QMs can be generated from the adducts. When the QMs are generated from the adducts in the presence of air there is very little chance to reverse back to the adduct structure since AHQ is rapidly oxidized by air to AQ. Our previous studies have shown that AQ is ineffective at inhibiting condensation reactions of QM's and phenolates. Consequently, the liberated QMs have no recourse except to condense (13 + 14 → dimers → polymers).

Further verification of the reversibility of adduct formation and decomposition was provided by the experiment outlined in Eq. (14). The adduct 39A was mixed with the chloroacetate 27 and heated at 100° in alkali in a nitrogen atmosphere to produce some adduct 39C, condensation products and mostly recovered adduct 39A.



(14A)



(14B)

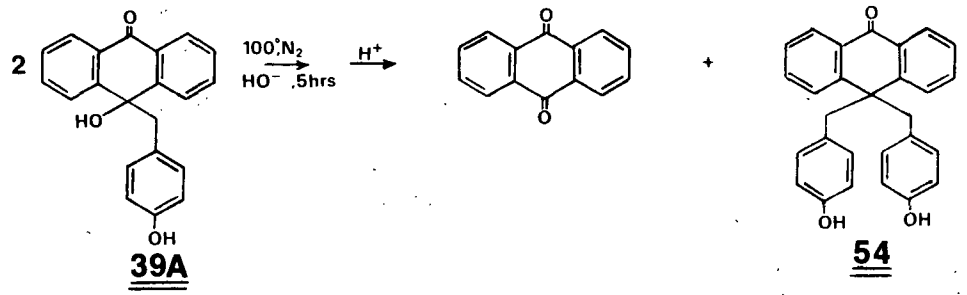
With a 1:1 ratio of reactants you might expect a 1:1 ratio of adducts 39A and 39C would be produced. However, if the equilibrium of adduct 39A with fragmentation products AHQ^{-2} and QM 24 lies largely on the side of the adduct, there will be very little AHQ^{-2} available for reaction with QM 14. The latter will then find itself in a sea of aqueous hydroxide and be converted to condensation products.

ALKALI REACTIONS AT ROOM TEMPERATURE IN AIR

All three adducts 39A-C were placed in separate Erlenmeyer flasks, containing water and hydroxide, and stirred in air at room temperature for 24 hours. Acidification led to a nearly complete recovery of the adducts. Apparently, the fragmentation of the adducts to AHQ and QMs requires some heating to be successful.

ALKALI REACTIONS AT 100° UNDER NITROGEN

Heating adduct 39A for several hours at 100° under nitrogen gave a 100% yield of AQ and a 93% yield of a 2QM-AHQ adduct 54. The yield calculations were based on the stoichiometry indicated by Eq. (15).

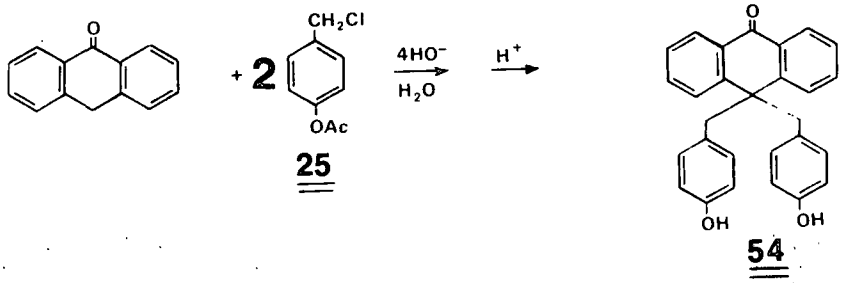


39A 54

(15)

The small amount of solid which we had isolated from the air cooks of 39A at 60-90° corresponded to compound 54. The probable reason that it was formed in the air cooks was that the reactions (in some cases) were started by heating in a nitrogen atmosphere before exposure to air. Those cooks done in air from the start did not give 54.

Purified 54 was characterized by (a) elemental analysis, (b) extensive spectral analysis and (c) synthesis from anthrone and the quinonemethide precursor 25, Eq. (16).



25 54

(16)

A possible mechanism for the formation of 54 from 39A is shown in Fig. 23. Several experiments have been attempted to verify this mechanism. The reaction described by Eq. (15) was performed a number of times, varying the reaction time, in order to determine the possible presence of the protonated forms of intermediate ions 74 and 75. Analysis of the derivatized reaction products by GC showed only 39A, 54 and AQ. Of course, lack of signals for the desired intermediates could be a result of matching retention times with the components already known to be present.

Authentic samples of the expected intermediates were sought. Since the proposed mechanism (Fig. 24) suggests that the intermediates arise by a reduction of the adduct 39A, we examined different ways of reducing 39A.

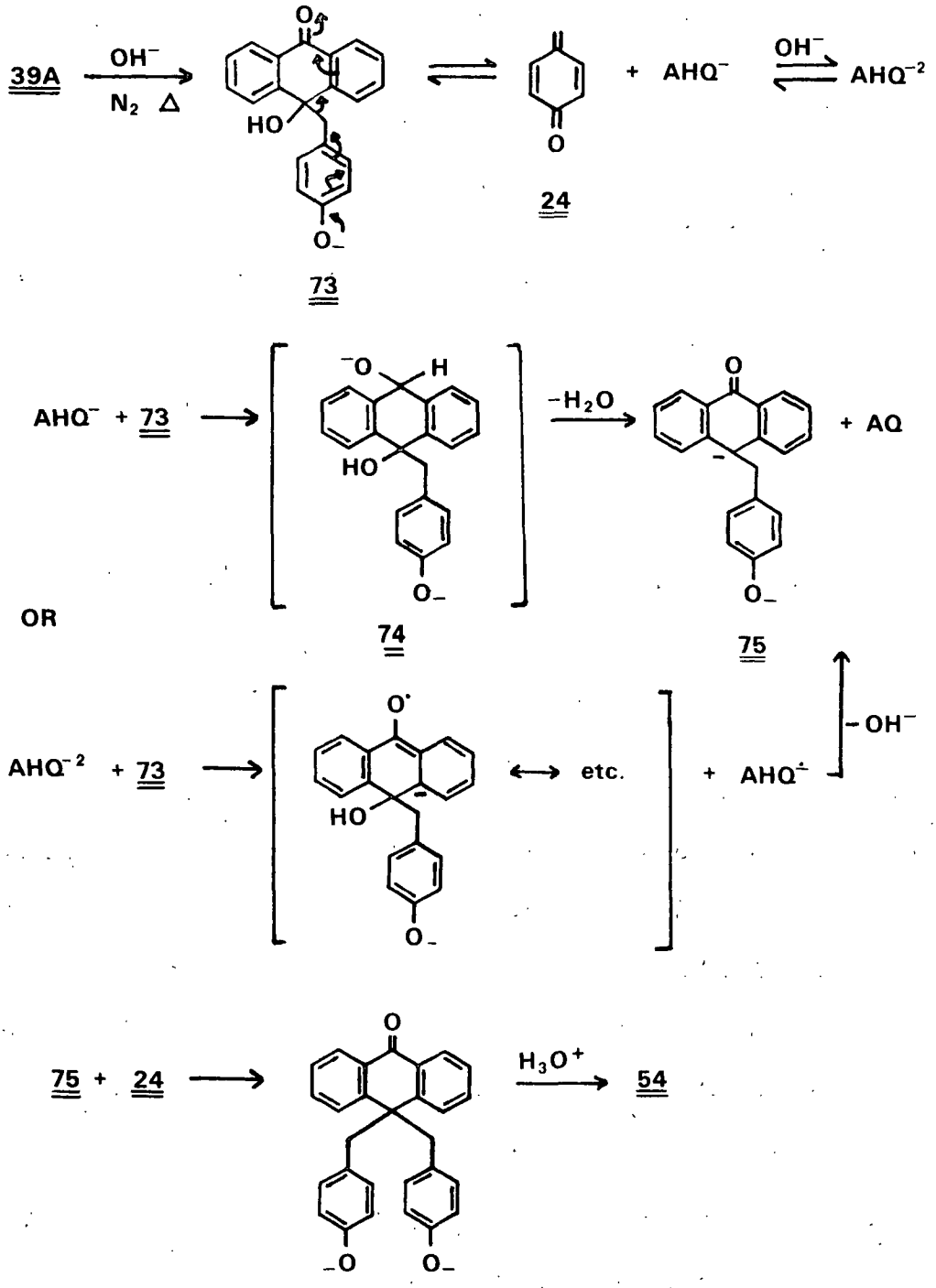
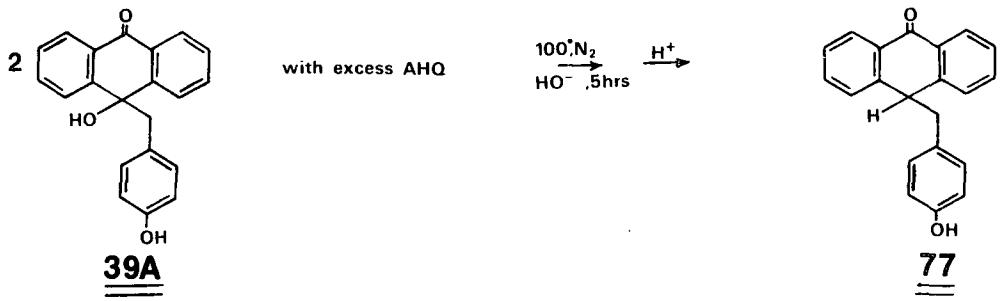


Figure 24. Proposed Mechanisms for the Formation of 54 from 39A

The most logical reducing agent for converting a ketone to an alcohol is hydride. Both lithium aluminum hydride in two different organic solvents and sodium borohydride in aqueous ethanol gave complex mixtures of products. Landucci has experienced similar problems in trying to reduce adducts with hydride (100). The messy reactions could be a result of the adduct's instability in base, and hydride is an excellent base.

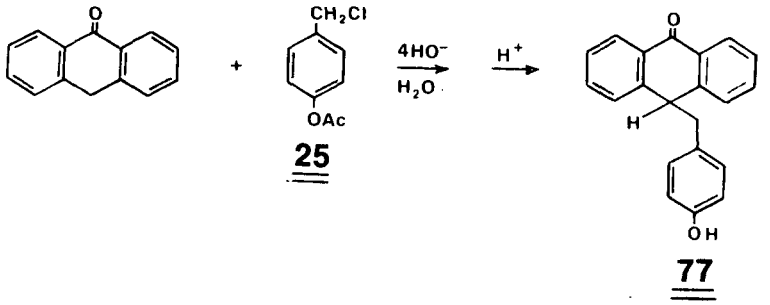
A second choice for the desired reduction was AHQ^{-2}, the proposed reducing agent in Fig. 24. Consequently, the reaction described by Eq. (15) was repeated, in the presence of a large excess of AHQ^{-2}. The idea was to reduce the formation of 54 by trapping the released QM with AHQ^{-2} (thus, regenerating 39A) and promote the reduction of 39A to intermediates 74 and 75, (Fig. 24). Again, the reaction afforded a mixture of products of which 77 appeared to be a component (based on NMR evidence) and increased in amount as the level of AHQ^{-2} increased from 2 to 4 to 8 equivalents [Eq. (17)].



39A **77** (17)

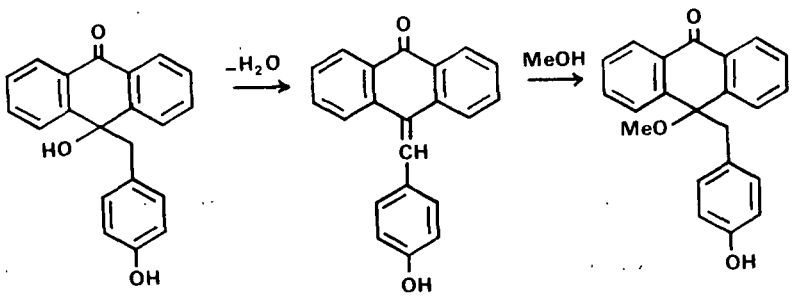
Actually the most straight forward way of producing 77 would seem to be the reaction of 1 equivalent of anthrone with 1 equivalent of QM [Eq. (18)]. However, when this reaction was tried, we experienced a complex product mixture. By means

of extensive purification, involving column chromatography, we were able to isolate and identify compound 77.



25 77 (18)

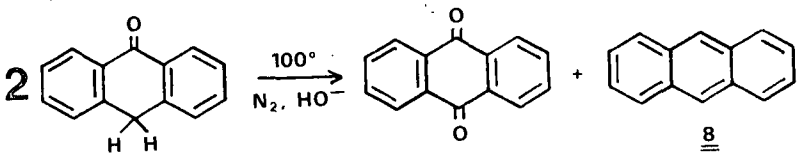
Some of the other products obtained in the reaction outlined by Eq. (18) were 54, AQ and 78. The latter probably arose during the several attempted methanol recrystallizations of the crude product. A logical pathway for the formation of 78 would be methanolysis of 39A, Eq. (19); however reflexing a sample of 39A in neutral methanol did not lead to 78 or cause any change. The proposed intermediate quinonemethide 79 has been prepared by treating 39A with p-toluenesulfonic acid; but has not been treated with methanol. A compound like 79 should be very susceptable to reactions with a nucleophile like methanol. Possibly traces of acid were present during the attempted methanol recrystallization mentioned above and 78 was thus formed.



39A 79 78 (19)

[Compounds 78 and 79 were characterized in the usual way — elemental and spectral analyses of recrystallized materials; see Appendix II.]

How can 39A and AQ be generated from the reactants shown in Eq. (18)? The procedure used was similar to that employed in most adduct reactions, namely, anthrone was heated in alkali with the chloroacetate 25 under nitrogen, cooled, exposed to air at room temperature in order to convert any AHQ to AQ, filtered to remove AQ and anthrone and the filtrate acidified to give the products. In a control reaction, in which the chloroacetate reactant was omitted, AQ was still produced. The question is whether AQ is formed in an anaerobic reaction, i.e., a disproportionation like Eq. (20), or during the oxidative work-up.



8 (20)

There is ample literature (115) which claims that anthrone and anthracene (8) can be readily oxidized to AQ by exposure of a warm (70°) alkaline solution of the material to a stream of oxygen. Interestingly, the autoxidation of anthracene gives AQ, but no anthrone, even at short reaction times (115). There appears to be some interesting chemistry in these oxidations, or disproporation, reactions of anthracene derivatives that warrants exploration. Dence and co-workers have detected anthracene, anthrone, and other reduction products of AQ in pulping liquors (49).

A sample of anthrone was heated for 3 hr in deoxygenated alkali under a nitrogen atmosphere, cooled, acidified under nitrogen, filtered and the collected

solid air dried. Only very little (few %) AQ was formed. This fact points out that many of our problems with complex product mixtures could have possibly been avoided if we had not allowed the alkaline reaction mixtures to be exposed to air. Of course, without this exposure, separation of products from AQ and anthrone would have been more difficult.

We have searched for anthracene (8) in the anthrone reactions that have produced AQ and found none. This appears to be further evidence that AQ arises principally from an oxidative reaction of ionized anthrone, rather than a disproportionation reaction [Eq. (20)].

Part of our problems with complex reaction mixtures in the preparation of 54 may be due to the reactivity of adduct 54. Its precursor dianion 75 may be in equilibrium with other more stable species or may be easily air oxidized.

ALKALI REACTIONS AT 173°

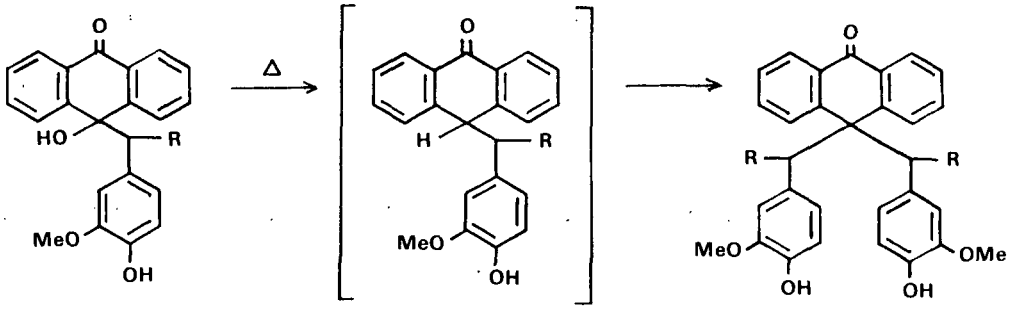
Adduct 39A has been subjected to duplicate (simulated) pulping experiments and qualitatively provided the same result. The adduct was mixed with alkali inside a titanium bomb under nitrogen for 2 hr at 173°, cooled and acidified. The water insoluble material was taken up in THF, derivatized with dimethyl sulfate and analyzed by GC. The most prominent signal was that due to AQ. There was a trace of 39A remaining but no appreciable quantity of the 2QM-AHQ adduct 54 in the complex mixture. [It is difficult to determine if the weak, broad, signals in the region where 54 elutes are due to 54 or other material.]

The alkali reactions at 100° demonstrated that QM-AHQ adduct 39A is not stable under these conditions. The cooks at 173° showed that the adduct 54

(derivable from 39A) is also unstable in very hot alkali. A more complete analysis of the products of the 173° cook may be pursued when the Institute's new GC/MS arrives.

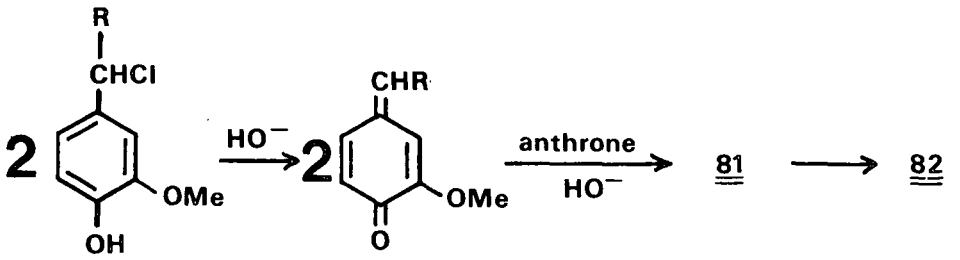
STERIC LIMITS OF ANTHRONE ALKYLATIONS

Thus far, the thermal reactions of the adducts 39A-C have mostly been done with 39A since it is the easiest to prepare and affords simpler products. Will these reactions [Eq. (21)] occur with other benzyl substituted adducts? If so, could this conversion of a QM-AHQ adduct to a 2QM-AHQ adduct be an important side reaction in AQ pulping?



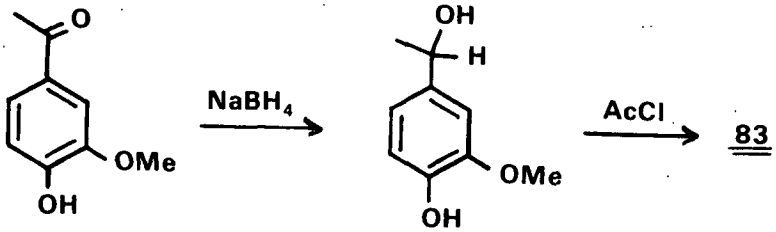
80 81 82 (21)

Since the second step of Eq. (21) involves alkylation of anthrone adduct with a QM, a potentially easy way to show if two bulky groups could be put on to an anthrone skeleton would be to simply alkylate anthrone twice [Eq. (22)].



(22)

The first series of compounds selected for study was R = methyl. The desired chloroacetate 83 was prepared by reduction of acetovanillone (85) to the alcohol 86 (116) and treatment of the latter with acetyl chloride [Eq. (23)].



85 86 (23)

Work is now in progress on the alkylation of anthrone with the chloroacetate 83. The preliminary results seem to indicate that a 1:1 ratio of reactants affords 81 (R = Me) and 2:1 ratio of reactants still gives mostly 81 (and condensation products). From this result it appears that the production of a 2QM-AHQ may be limited to simple adducts possessing unsubstituted benzyl carbons. If this is true, the likelihood of producing 2:1 QM to AHQ adducts of lignin, where the benzyl carbon of the QM is substituted by a fairly large group, appears remote.

SIGNIFICANCE OF QM-AHQ ADDUCTS

What role do QM-AHQ adducts play in the delignification of wood? Are they products that form momentarily and through reverse to reliberate AHQ and a QM and do not really contribute to the process of delignification at all? Or are these adducts crucial to the delignification process (fragmentation and condensation) and responsible for AQ losses during pulping? A case can be made for this latter view based on model studies. This case will be presented here.

In the Introduction Section, I discussed some of the chemistry of lignin reactions and presented the view that quinonemethides play a central role in both fragmentation and condensation reactions of lignin. For example, the key to rapid delignification appears to be fragmentation of the β-aryl ether linkage after a quinonemethide has been formed (Fig. 6 and 7). The fact that AQ, in the form of AHQ, is a delignification accelerator suggests that a process is involved which leads to efficient cleavage of β-aryl ether bonds.

Figure 25 shows schematically how QM-AHQ adducts could offer an alternate pathway for cleavage of β-aryl ether bonds. The actual details of how the adducts

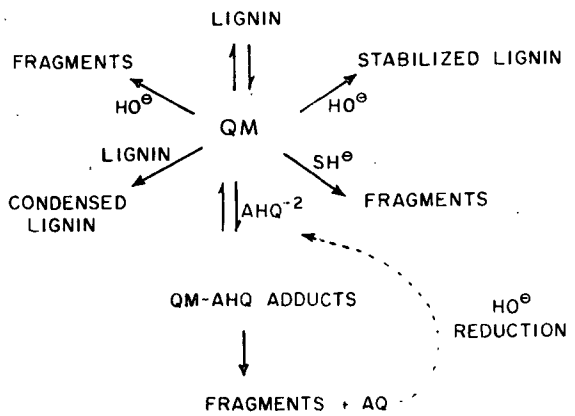


Figure 25. Postulated Reactions of Quinonemethide Intermediates (QM) Which Have β-aryl Ether Substituents

could cause fragmentation and regnerate AQ are presented in Fig. 26. Landucci (74) has evidence from model studies that a process like this is possible. Note that one of the products is a vinyl phenol, a product seemingly peculiar to AQ systems (70). In this mechanistic picture, the two charges on AHQ^{-2} are transmitted to a lignin QM causing the formation of two (fragmented) phenolate ions and AQ. The AQ presumedly becomes reduced to AHQ by reactions with carbohydrates and the catalytic process continues with a new QM.

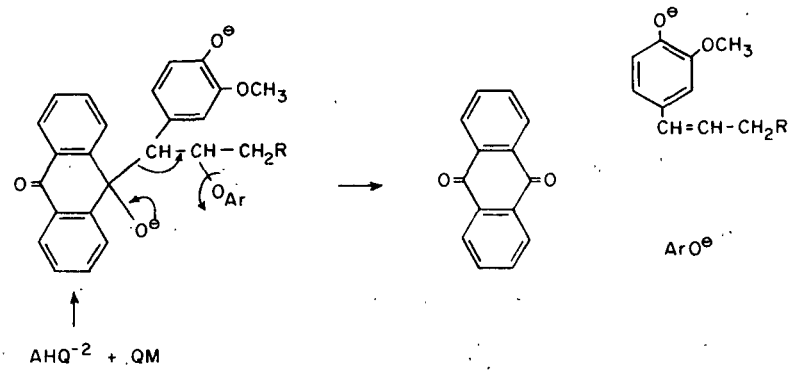


Figure 26. Postulated Breakdown of QM-AHQ Adducts of Natural Lignin to Fragmented Products and Anthraquinone

Not all of the quinonemethides derived from lignin have β-aryl ether groups present. Possibly, quinonemethides of this type are responsible for a significant portion of the lignin condensation reactions observed in the kraft pulping process. Both hydroxide and sulfide could add to this type of QM, but the resulting products have no further reactions available to them, except to return to the original QM. The established equilibria would lower the concentration of QM's and, thereby, decrease lignin condensation reactions, Fig. 27.

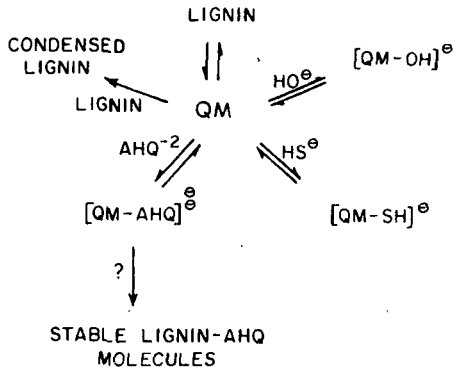


Figure 27. Postulated Reactions of Quinonemethide Intermediates Which do not have β-aryl Ether Substituents

Our work has shown that adducts form from AHQ and QMs in alkali and that the reactions are reversible at elevated temperatures. If the equilibria for these reactions lie strongly in favor of the adducts (more so than the hydroxide and sulfide — QM equilibria), then quinonemethide condensation reactions would be greatly disfavored, Fig. 27. There is some evidence that QM + AHQ $\rightleftharpoons$ adduct equilibrium does largely favor the adduct; see Eq. (14) and related discussion.

An alternative, or complimentary, way in which QM-AHQ adducts may become involved in retarding lignin condensation reactions is also shown in Fig. 27. The adducts may drain away the QMs to some type of stable molecule. There is no direct evidence that adducts can do this; however, there is evidence that AQ and/or AHQ become bound to water soluble lignin during the course of pulping (51,78). Also, as mentioned in the Introduction Section, addition products of AHQ and lignin by-products have been observed in black liquors (79,80).

Assuming that condensed lignin contributes to "residual" lignin it should be possible to produce "low lignin" pulp more easily by an AQ process than by a conventional process. In some related project research (117) at the Institute on

loblolly pine, low lignin pulp, having reasonable strength properties, was produced by a kraft-AQ process. The lignin from this pulp was more easily removed by conventional bleaching techniques than the lignin from a standard kraft pulp. However, the "low-lignin" pulp was somewhat difficult to bleach to a high color brightness. Whether or not AQ pulps are more easily bleached in general is still a matter of concern; there appear to be substantial differences when comparing kraft and kraft-AQ pulps with regard to the species of wood and type of bleaching used (41-44).

CONCLUSIONS

The following conclusions summarize the present state of knowledge of the role of anthraquinone in alkaline reactions of wood and model wood components:

1. Increased pulp yields can be attributed to carbohydrate stabilization and milder cooking conditions.
2. Anthraquinone, or its reduced form, when used in catalytic amounts, increases the rate of delignification dramatically.
3. AQ oxidizes carbohydrates, giving rise to AHQ, stabilized carbohydrates and increased chain cleavage.
4. AHQ reacts with lignin intermediates (quinonemethides) to give adducts.
5. QM — AHQ adducts rapidly fragment when appropriate β-aryl ether groups are present.
6. QM — AHQ adducts divert some quinonemethide species away from the condensation reactions.
7. The losses of AQ during pulping can be attributed to formation of alkali stable products derived from AHQ reactions with lignin intermediates or lignin by-products.

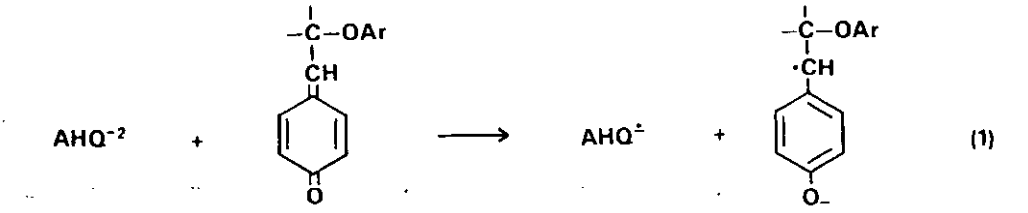
FUTURE WORK

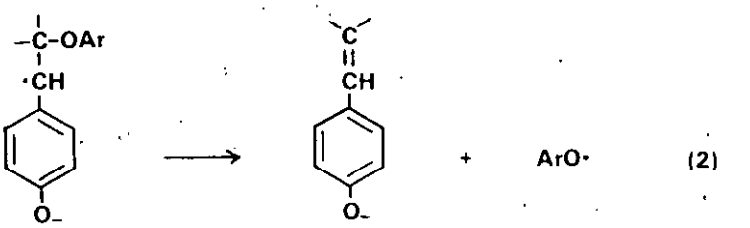
Is it possible that the quinonemethide intermediates of actual lignin are too bulky to form QM-AHQ adduct structures? Are adducts a requirement for efficient delignification? The proposed mechanism of AHQ induced lignin fragmentation involving adduct intermediates (Fig. 26) represents, in essence, a way for AHQ^{-2} to transfer its charge to QMs of lignin, causing fragmentation to two phenolate ions and production of AQ. Do bonds have to actually form? Could AHQ^{-2} simply transfer two electrons to a QM, causing fragmentation and AQ production, without actual bond formation?

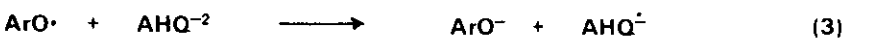
Future research efforts in Project 3370 will be directed toward finding answers to these questions. We will be trying to distinguish between rapid bond formation-fragmentation *vs.* simple electron transfer. Scheme I outlines a way in which electron transfer reactions between water soluble anthraquinone derived species can account for carbohydrate stabilization and lignin degradation. Note that the summation of equations 1-4 of Scheme I, namely Eq. (5), contains no AQ derivatives; the AQ compounds are only catalysts.

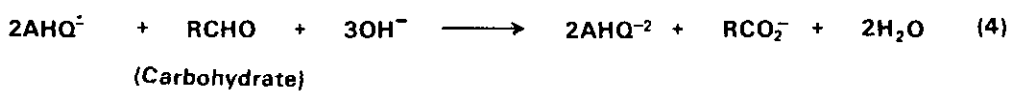
Several of the intermediates proposed in Scheme I are radical anions. Radical anion reactions can generally be quenched by nitroaromatic inhibitors. We intend to study the influence of radical anion inhibitors on soda/AQ reactions of wood and model systems to determine any differences in degrees of lignin fragmentation and condensation.

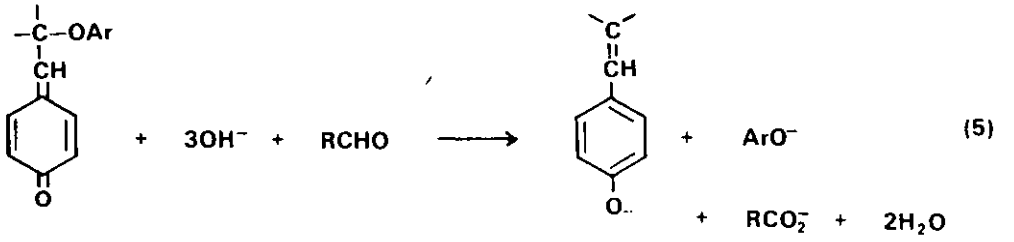
Electron transfer reactions differ from bond formation reactions in their steric requirements. Unlike the latter, electron transfer reactions are generally insensitive to steric factors. Consequently, a second approach we intend to take in studying the importance of electron transfer reactions is to











Scheme I. Proposed Electron Transfer Mechanism of Action of Anthraquinone Derived Materials During the Pulping of Wood

determine the effects of steric bulk on the fragmentation of model lignin compounds.

Why is it important to prove or disprove the electron transfer theory of action of AQ in pulping systems? The answer is obvious. If we know the actual fine details of how AQ acts, we can use this information to (1) improve AQ-pulping, such as finding ways to improve pulp strengths, (2) search for the "ultimate" catalyst, (3) better understand our present processes and (4) devise ways to reduce residual, condensed, lignin in pulp and, thereby, facilitate less costly bleaching sequences.

EXPERIMENTAL

A complete description of the experimental details of the research discussed herein would make this report considerably longer than it already is; consequently, it will be omitted. The intentions of this author are to publish our pertinent results in scientific journals. An experimental section will accompany these publications. Of course, members wishing earlier details may contact this author. Actually, many of the important experiments are described in fair detail in the body of this report; spectral and elemental analysis data are either provided in the text or appendices.

ACKNOWLEDGMENT

The contributions of Donaline Shepard to much of the experimental work described here, to writing certain sections and to proofreading this report have been invaluable to the progress of this project. The assistance of Hugh Corbett to the experimental work involving the oxidative reactions of anthraquinones was also important. The continuing support and input of Earl Malcolm to this project is much appreciated.

APPENDIX I

ANALYTICAL METHODS FOR DETERMINING AQ

A number of small-scale soda and kraft cooks on loblolly pine were carried out to provide pulp and liquor samples for AQ analysis. Yields and kappa numbers were determined and, as indicated in Table V, showed the beneficial effects of AQ. Two methods of analysis for AQ were tried, gas chromatography (GC) and polarography, neither of which was completely satisfactory for both soda and kraft samples.

GC METHOD

The pulps were air-dried and then extracted with toluene. Benzil was added as an internal standard to the toluene extract before it was concentrated and analyzed by GC. Typically, 2-4% of the original AQ ended up in the pulp as shown in Table V. A control pulp (no AQ in the cook) was spiked with a known amount of AQ, extracted and analyzed; 90% of the AQ was recovered.

Analysis of liquors was not as simple. Even after 3 days of continuous extraction with toluene, additional AQ was extracted from liquor samples. Consequently, the values in Table V for liquor analyses should be considered minimum values. Also, it was found that fine solids, which were normally filtered from the liquors before extraction, contained a substantial amount of AQ, roughly 20-30% of the original AQ. These solids were not analyzed by the GC method; this partially accounts for the low values of AQ recovery obtained by the GC method.

POLAROGRAPHIC METHOD

Anthraquinone is readily reduced at a dropping mercury electrode and its reduction potential (ca. - 0.65 to - 0.75 volts depending on pH) falls in a region

TABLE V

ANTHRAQUINONE PULPING OF LOBLOLLY PINE

	Entry	Additive, %	Yield, %	Kappa No.	AQ in Pulps, % of original		AQ in Liquors, % of original	
					GC	Polarography	GC[c]	Polarography[d]
Soda[a]	1	--	59.6	125	--	--	--	--
	2	AQ, 0.25	51.2	45	1.6	--	8.5	50.7
	3	AQ, 0.50	50.4	40	4.7	--	9.7	32.3
	4	AQ, 1.0	51.4	30.5	4.2	4.2	19.5	45.7
	5	Glucose, 10; AQ,1.0	53.3	38	2.1	--	8.8	36.4
	6	Vanillin, 10; AQ,1.0	54.0	54	4.4	--	15.6	38.4
	7	--	47.3[e]	36.3[e]	--	--	--	--
Kraft[b]	8	--	49.7	32	--	--	--	--
	9	AQ, 0.2	50.1	32	1.5	--	10.8	--
	10	AQ, 0.4	50.9	28	1.3	--	8.7	--
	11	AQ, 0.8	50.8	224	3.1	--	10.6	--

[a]Soda cook conditions: 20% NaOH as Na_2O, liquor ratio 4 cc/g, time to temperature = 90 min, time at 173°C = 45 min.
[b]Kraft cook conditions: active alkali 18%, sulfidity 28%, liquor ratio 4 cc/g, time to temperature = 90 min, time at 173°C = 75 min.
[c]Analysis of filtered liquor.
[d]Analysis of filtered liquor plus liquor solids.
[e]Average of 6 runs, cooked at 173°C for 240 min.

where most organic compounds do not reduce. The polarographic method offers several advantages in the analysis of AQ: (1) it is quite sensitive, i.e., 1 ppm can be detected, (2) it analyzes the composite of AQ and AHQ and (3) it can be performed on straight liquors, no solvent extractions are necessary. Its disadvantages are: (1) levels above 5 ppm AQ can not be determined quantitatively because of the limited solubility of AQ in the electrolyte solution and (2) the technique does not appear to be applicable to kraft liquors where sulfur species interfere.

Differential pulse polarography was the method of choice for the analyses since peak height can be related to the concentration of AQ. A calibration curve was prepared by recording polarograms for an aliquot of the supporting electrolyte (0.1M $LiCl_2$ in 50% ethanol) spiked with successive aliquots of a standard AQ solution. Peak differential current (μA) was then plotted versus concentration of AQ (ppm).

Pulps were extracted with toluene as in the GC method. A small aliquot of the extract was allowed to evaporate to dryness. The residue was redissolved in the polarographic electrolyte solution and analyzed.

Soda liquors were filtered before analysis. The dried filter papers were extracted with toluene and the extracts analyzed in the same manner as those from pulps. An aliquot of the filtered liquor was neutralized, diluted with the electrolyte solution and analyzed. At concentrations greater than 5 ppm in this electrolyte, AQ can precipitate; therefore, dilution factors were chosen to keep the concentration of AQ in the 1-5 ppm range.

The values in Table V for the polarographic analysis of liquors are the sum of the AQ found in the liquor solids and the filtered liquor.

Kraft liquors contain large amounts of sulfur compounds which have reduction potentials in the same range as AQ. It was possible to shift the reduction potentials of the sulfur compounds and AQ by adjusting the pH. Even though some separation of peaks was achieved, the concentration of sulfur compounds was so much greater than that of AQ that quantitative measurement of AQ was not possible. Various methods for removal of the sulfur compounds from the liquors were tried, none of which were very satisfactory.

CONCLUSIONS

Based on our limited exposure, polarography appears to be the method of choice for analyzing for AQ in soda pulps and liquors. The research group at PPRIC has had good results with this technique (78). The GC method may be the only reasonable method for analyzing kraft pulps and liquors. Groups at Washington, (76) Syracuse (49) and CIL (77) have spent much more time perfecting the GC method than we. As a note of caution, some wood components elute at the same place as AQ, so that the GC analysis should probably be coupled with a mass spectrometric analysis (77).

The analyses show that a considerable amount, roughly one-half, of the original AQ cannot be accounted for in the resulting pulp and liquors. Evidence is mounting that some AQ becomes bound to soluble lignin material (51,78). Also, some AQ is converted to anthrone, anthracene and 9,10-dihydroanthracene (49). The slow release of AQ upon continued extraction of liquors may be due to slow oxidation of AHQ, anthrone, etc., to AQ and a slow unbinding of the AQ from the lignin.

APPENDIX II

OXIDATION REACTIONS OF ANTHRAQUINONES

Various studies have shown that AQ and anthraquinone monosulfonate (AMS) oxidize carbohydrates, converting reducing end groups (aldehydes) to aldonic acid end groups (carboxylic acids). Competing with the oxidative reactions of carbohydrates is the alkaline "peeling" reaction in which successive monomeric units are lost from the polymer chain, causing substantial yield losses. Aldonic acid end groups are relatively stable to alkali so that an oxidized carbohydrate is a "stabilized" carbohydrate. The enhanced yield gains when pulping in the presence of AQ or AMS have been attributed to carbohydrate stabilization.

CELLOBIOSE/AMS REACTIONS

We became interested in studying the relative rates of peeling vs. oxidation of polysaccharides by AQ or AMS. The peeling reaction is known to be a very rapid process and would, therefore, require special equipment to study. Fortunately, the Institute has the necessary equipment, namely a fast flow reactor capable of measuring reactions in the millisecond range, and some experienced personnel in this area (118). This equipment is only capable of handling homogenous solutions. Therefore, a water soluble carbohydrate, cellobiose, was chosen as the substrate for the study. Cellobiose has frequently been used as a "model" carbohydrate.

In studying the rate of a particular process, you generally follow the disappearance of starting material and/or the appearance of an appropriate product as a function of time. Figure 28 outlines the anticipated major alkaline and oxidative reactions of cellobiose. It was felt that AQ or AMS would increase the rate of disappearance of cellobiose and rate of appearance of cellobionic and

glucosylmannonic acid (aldonic acid type disaccharides) in comparison to a control reaction which contained no added oxidant.

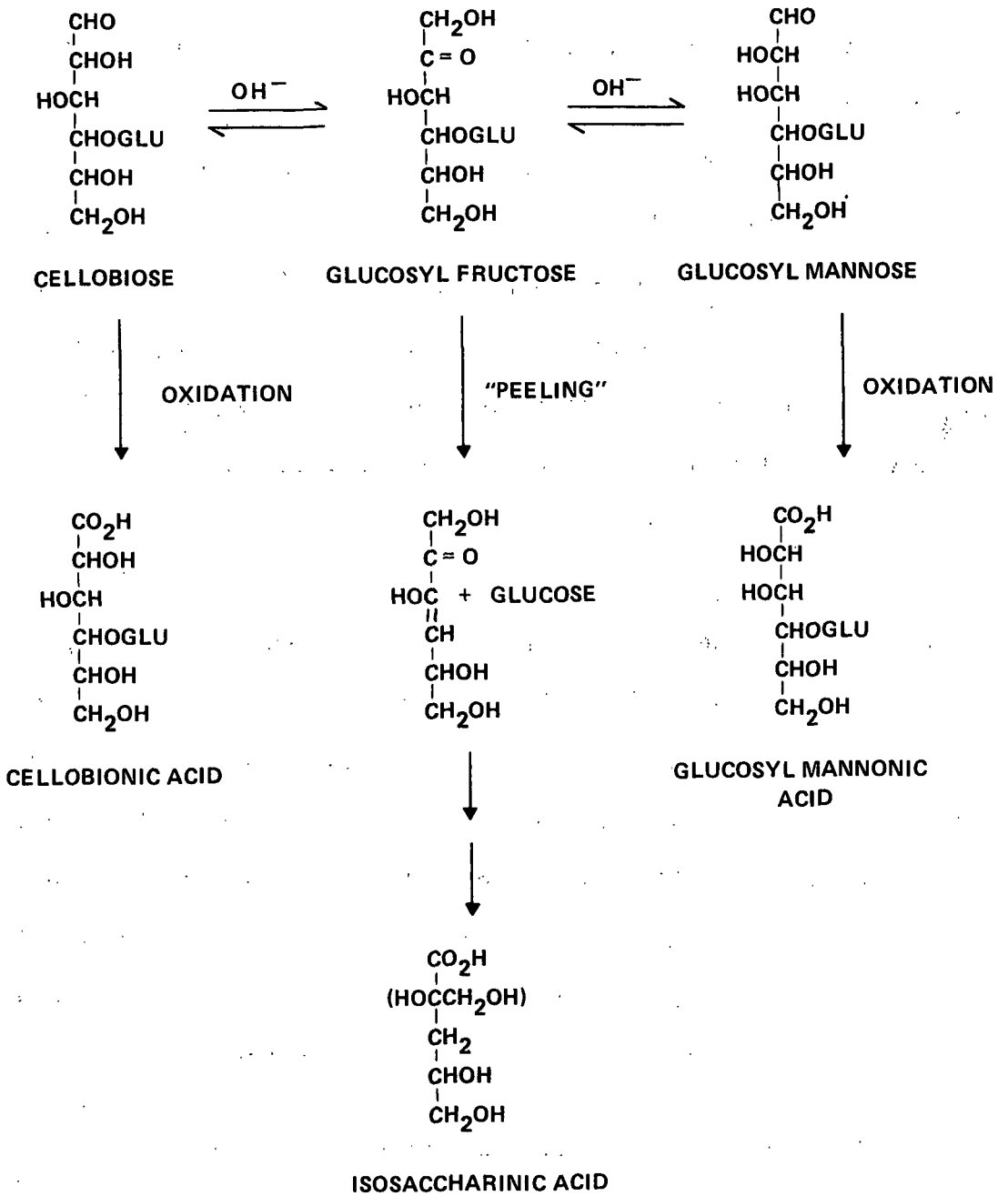


Figure 28. Some Oxidative and Alkaline Reactions of Cellobiose

The oxidant chosen for this study was AMS, rather than AQ. The latter has a very low water solubility and large levels of oxidants were required. The equipment and method of analysis could probably not cope with additional additives, like lignin, which would be necessary to the use of AQ or AMS at catalytic levels. The ratio of reactants was 1 part cellobiose to 1 part AMS to 3 parts sodium hydroxide (on a molar basis). Duplicate runs of 5, 15 and 30 minutes duration were performed at 100°C, in a nitrogen atmosphere, with one set containing AMS and the other no AMS. After quenching and removal of solvent, the products were silated and analyzed by GC. The pH drop during the course of the reactions was from 12 to 10.5-11.0.

Our main interest was to observe changes in the levels of disaccharide components between the control and AMS runs. Figure 29 shows the disaccharide region (expanded and enlarged) of the gas chromatograms for control and AMS runs of 5 minutes duration. The peaks designated by the arrows in the figure had the same retention time as the indicated aldonic acids. [Similar retention times are not, however, sufficient proof of identity.]

None of the peaks in the disaccharide region were rigorously identified because the close similarity of the control and AMS runs negated much of the value of the study. The AMS run showed a somewhat greater abundance of disaccharide type products and cellobionic acid. The appearance of oxidation products from the AMS run was anticipated, but to get the same oxidation products at comparable levels in the control run was puzzling. Even though attempts were made to exclude molecular oxygen, some may have been present and responsible for the oxidation products.

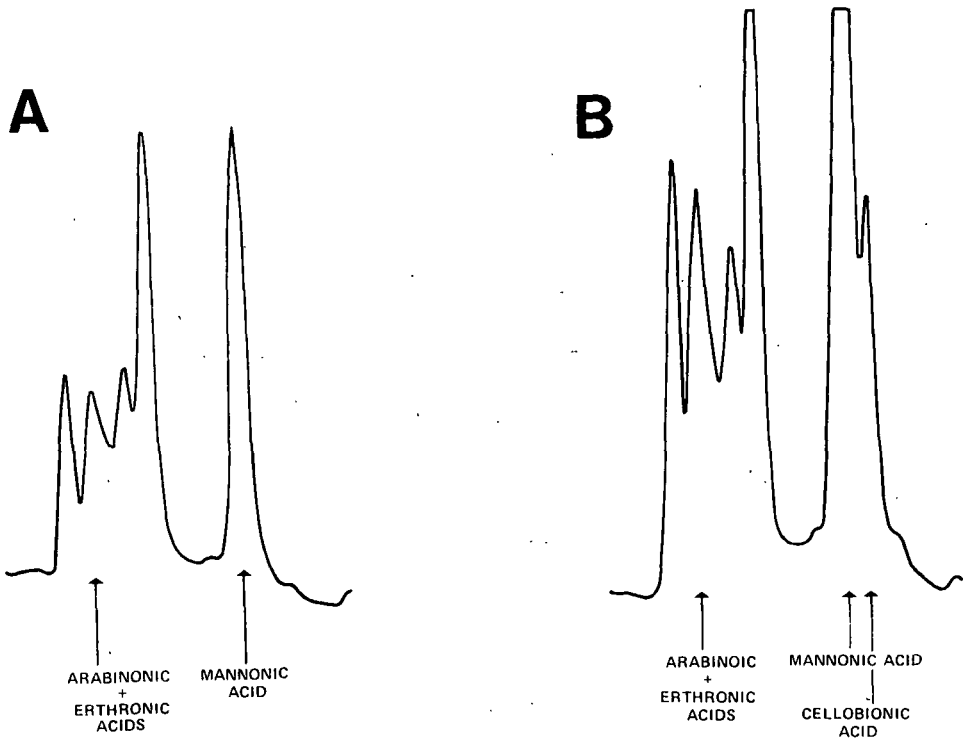


Figure 29. Gas Chromatograms of the Disaccharide Region for the Alkaline Reaction of Cellobiose at 100° After 5 Minutes for (A) No Additive and (B) 1 Equivalent of AMS

The 5, 15 and 30 minute runs were all very similar, suggesting that the reaction was basically concluded before 5 minutes had been reached. Cellobiose was not observed in any of the reaction products.

The low retention time region of the gas chromatograms of the AMS and control runs showed large differences in the relative proportions of some of the components (Fig. 30). Tentative peak assignments for the chromatograms were made based on identical retention times with known and synthesized compounds. The most dramatic differences were in the levels of deoxypentonic acids and isosaccharinic acids; the former were quite abundant in the AMS runs, the latter in the control runs.

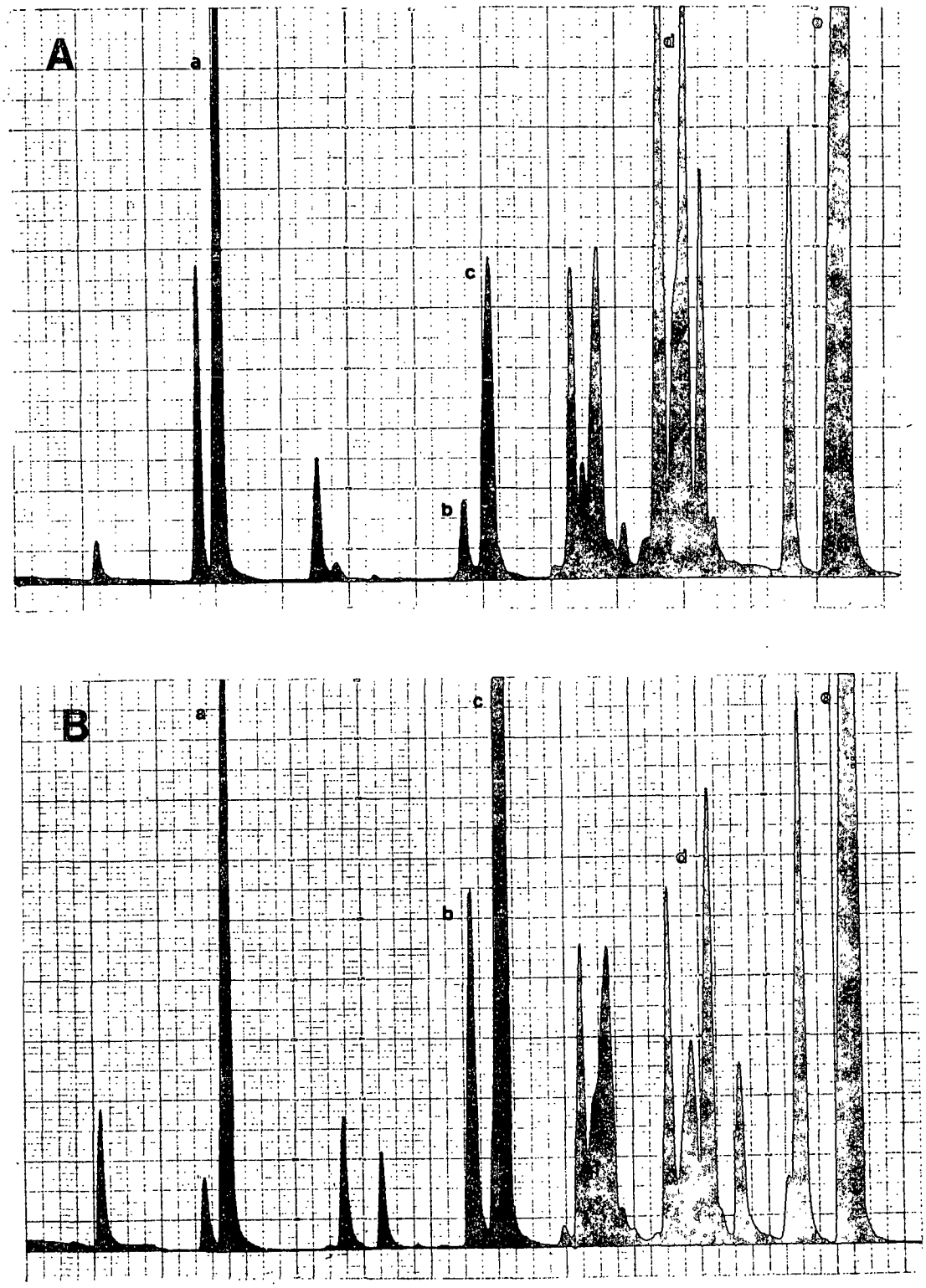


Figure 30. Gas Chromatograms of the Monosaccharide Region for the Alkaline Reaction of Cellobiose at 100° After 5 Minutes for (A) No Additive and (B) 1 Equivalent of AMS, After Trimethylsilyl Derivatization. The peak assignments, based only on comparable retention times, are as follows: (a) 2,3 or 2,4-dihydroxybutric acid, (b) 2-deoxypentonic acid, (c) 3-deoxypentonic acid, (d) region of iso and metasaccharinic acid isomers and (e) inositol, the added internal standard

A possible explanation of these differences is that AMS is capable of oxidizing the "peeling" fragment 87 to 3-deoxypentonic acid, diverting 87 from its normal course of conversion to an isosaccharinic acid. Figure 31 outlines these reactions. Lowendahl and Samuelson (56) have noted small increases in 3-deoxypentonic acid in alkaline reactions of cellobiose containing low levels of AQ; no explanation was given, however. The observed effect is much more pronounced in our studies, probably because of the high levels of AMS employed.

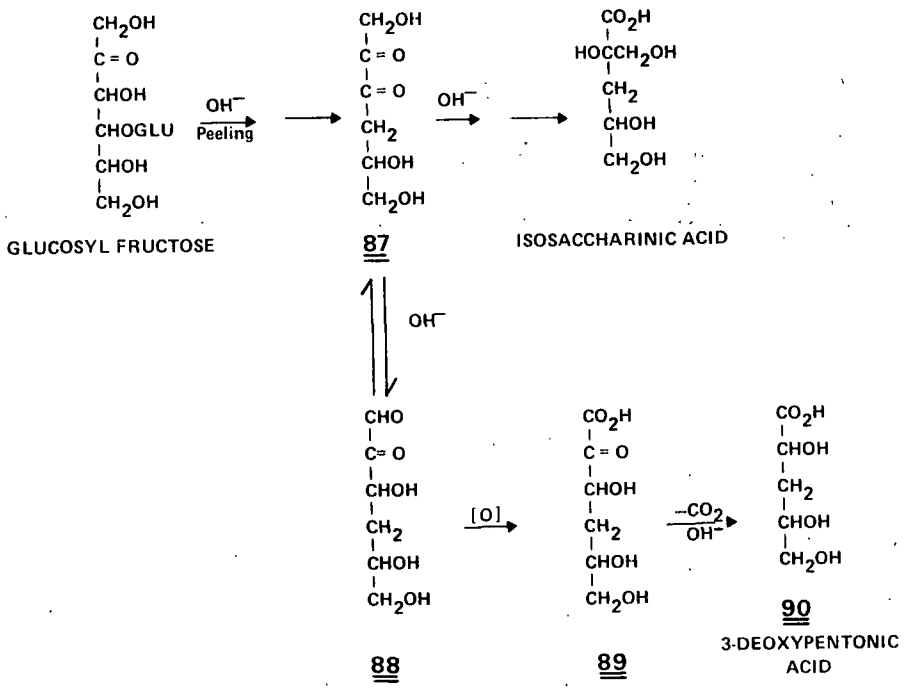


Figure 31. Production of 3-Deoxypentonic Acid by AQ Oxidation

These results indicate that the reactions of AMS (and AQ) with "peeling" intermediates are major pathways; they appear to be more prominent than reactions with intact carbohydrates. This brings up the question as to how AQ is able to stabilize cellulose and hemicelluloses (i.e., increase pulp yields) when so much of it must be consumed by reactions with carbohydrate fragments. Could there be

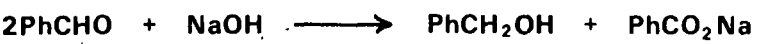
carbohydrate reactions which also regenerate AQ? Does oxidation and "peeling" of insoluble polymeric carbohydrate proceed at rates quite different from that of homogeneous solutions?

A set of control and AMS runs was also done at 150° with time intervals of 1/2, 1, 10 and 60 sec. Analysis of silated reaction products by GC showed few differences between the control and AMS runs, even in the low retention time region. The 1/2 and 1 sec runs showed glucose, but not cellobiose; it is known that glucose, a peeling product, is less reactive than cellobiose toward alkali (119). The disaccharide region in the GC of the 1/2 and 1 sec products was very similar to that shown in Fig. 29. The 10 and 60 sec products contained practically no disaccharide components; apparently, these materials were not stable at 150°. In fact, the 60 sec runs were void of GC signals. The 10 sec control and AMS runs were weak in signals, but showed the greatest (albeit small) differences.

With further refinement in techniques and reduction in reaction times, it might have been possible to find conditions which would allow the study of the relative rates of carbohydrate oxidation (by AMS) and "peeling". However, the odds of success in a reasonable time period were not good; consequently, this area of research was abandoned in favor of faster moving, more fruitful, areas.

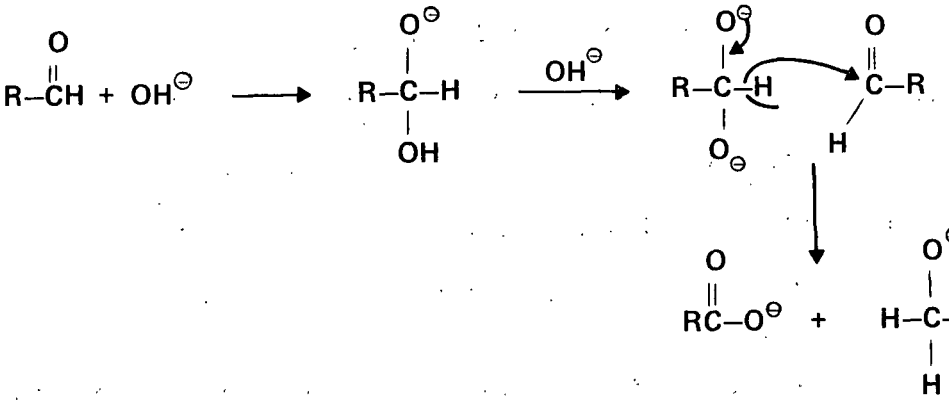
CANNIZZARO REACTION

A question raised earlier was "Is there a way in which carbohydrates can convert AHQ to AQ?" In pursuit of an answer to this question, we looked into the reactions of benzaldehyde with AQ and AMS. We were trying to observe the influence of these additives on a reaction of benzaldehyde known as the Cannizzaro reaction (129) [Eq. (24)].

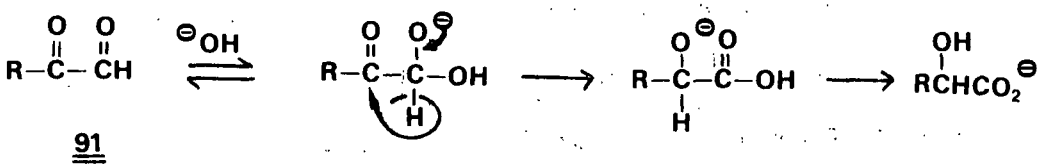


(24)

The mechanism of the Cannizzaro reaction is still under active investigation (121). Deuterium labeling studies have shown that a hydrogen is transferred from one aldehyde to another, probably *via* the mechanism outlined in Eq. (25) (121). Some of the degradation reactions of carbohydrates are believed to involve intramolecular Cannizzaro reactions [Eq. (26)].



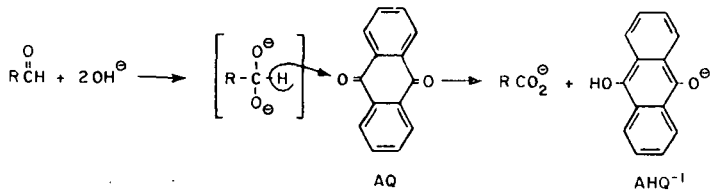
(25)



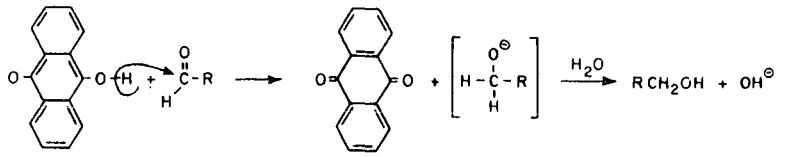
(26)

The ability of AQ to oxidize aldehyde groups of carbohydrates may be related to a "cross" Cannizzaro mechanism [Eq. (27)]. The AHQ^{-1} produced in this kind of reaction could presumably transfer a hydride back to another aldehyde regenerating AQ and reducing the aldehyde group [Eq. (28)]. In essence, AHQ^{-1} would act

as an intermediary in a regular Cannizzaro reaction. The summation of Eq. (27) and (28), including NaOH and the transfer of a proton between RCH_2O^- and RCO_2H, gives Eq. (24).



(27)



(28)

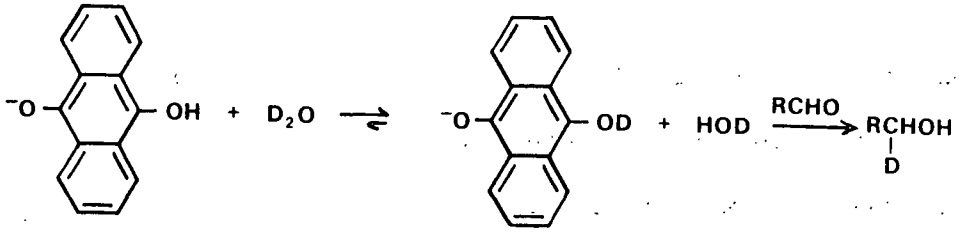
Samuelson claims to have observed only trace amounts of reduction products derived from carbohydrates in AQ reactions of cellulose (60). Reduction of small carbohydrate fragments may be difficult to detect. The instability of α-keto aldehydes, like 91, make them prime candidates for both oxidation and reduction reactions.

We decided to take a quick look at the reactions of benzaldehyde with AQ and AMS under Cannizzaro conditions, namely 50% aqueous NaOH. Benzaldehyde was chosen because it has been extensively studied in the past and the product analysis would be simple. In retrospect, it may have been a poor choice because: (a) it lacks the water solubility of a carbohydrate and (b) has to be extremely pure to get good results (121).

Our initial results were quite encouraging. Benzaldehyde was mixed with 50% NaOH in a nitrogen atmosphere alone, with a trace of AQ and a trace of AMS for 20 minutes. The AQ run produced twice as much benzoic acid and benzyl alcohol as the control run and AMS, which is water soluble, produced 4 times as much of each product.

The base concentration, temperature and time were varied to see what influence changes in reaction conditions might have on the course of the reaction. During this study, it was observed that the AMS reactions did not always produce greater yields than the control. There seemed to be an induction period associated with the reactions which made data interpretation difficult. The characteristic red color of a charged AHQ (or AHMS) was seen in all the runs containing additives.

One possible way to determine if AQ or AMS is acting as an intermediate in the Cannizzaro reaction is to conduct the reaction in D_2O as the solvent and using NaOD as the base. If AHQ^{-1} is present and acting as an intermediate, you would expect an exchange reaction to occur which would eventually lead to deuterium incorporation into the alcohol product [Eq. (29)]. The alcohol formed in a Cannizzaro reaction carried out in D_2O has been shown to not contain any deuterium in the $-CH_2-$ group (120).



(29)

A reaction was run in which 1 mL of benzaldehyde, 4 mL of 40% NaOD in D_2O and 0.05 g of AMS-2 were stirred at 17° for 2 hr under nitrogen, quenched and the organic neutrals analyzed by GC and ^1H-NMR. The product was a 30:70 mixture of PhCHO and $PhCH_2OH$, with no detectable deuterium incorporation in the latter. Interestingly, a control, which contained no additive, gave a 10:90 mixture of PhCHO and $PhCH_2OH$. From these results it appears that AQ or AMS is not capable of transferring hydrogens to benzaldehyde in the manner indicated by Eq. (27) and (28).

There still remains the observation that AMS and AQ *generally* promote the Cannizzaro reaction of benzaldehyde. Can there be electron transfer, rather than hydrogen transfer, between AQ and benzaldehyde that promotes the reaction? Many of these reactions should be repeated using ultrapure benzaldehyde or a water soluble aldehyde, preferably a ketoaldehyde, to verify our findings and extend the scope of the study. However, time and man-power restrictions have prevented further study in this area at the present.

APPENDIX III

SUPPORTING NMR DATA FOR THE STRUCTURE PROOF OF 10-HYDROXY-10-(4'-HYDROXYBENZYL)-9(10H)-ANTHRACENONE (39A): ORIGINAL SPECTRA

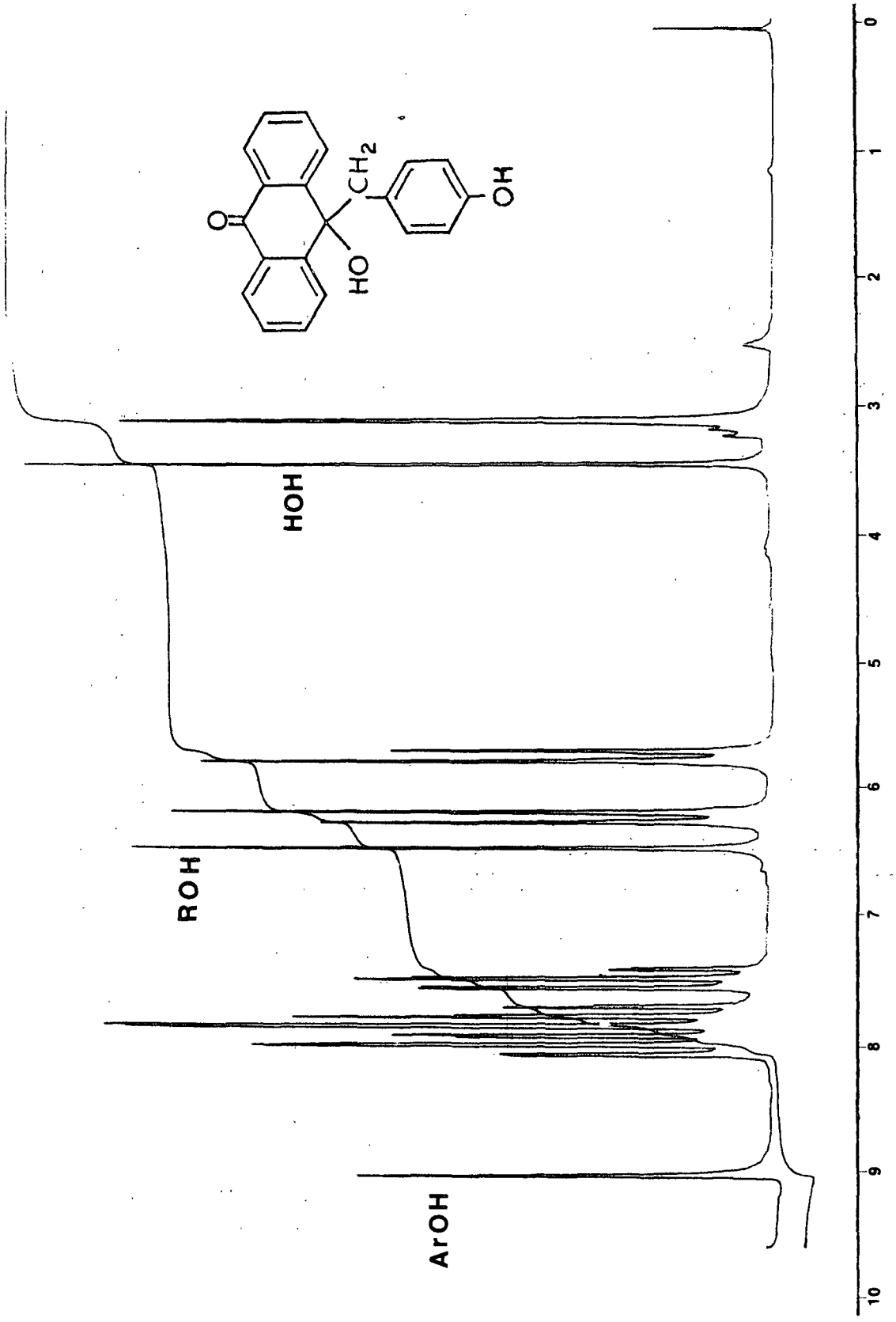


Figure 32. ^{1}H-NMR Spectrum of 10-Hydroxy-10-(4'-hydroxybenzyl)-9(10H)-anthracenone in DMSO. The Signals Marked H_2O, ROH and ArOH Shifted or Were Lost When D_2O was added to the Sample. Detailed Assignments are Made in Table III

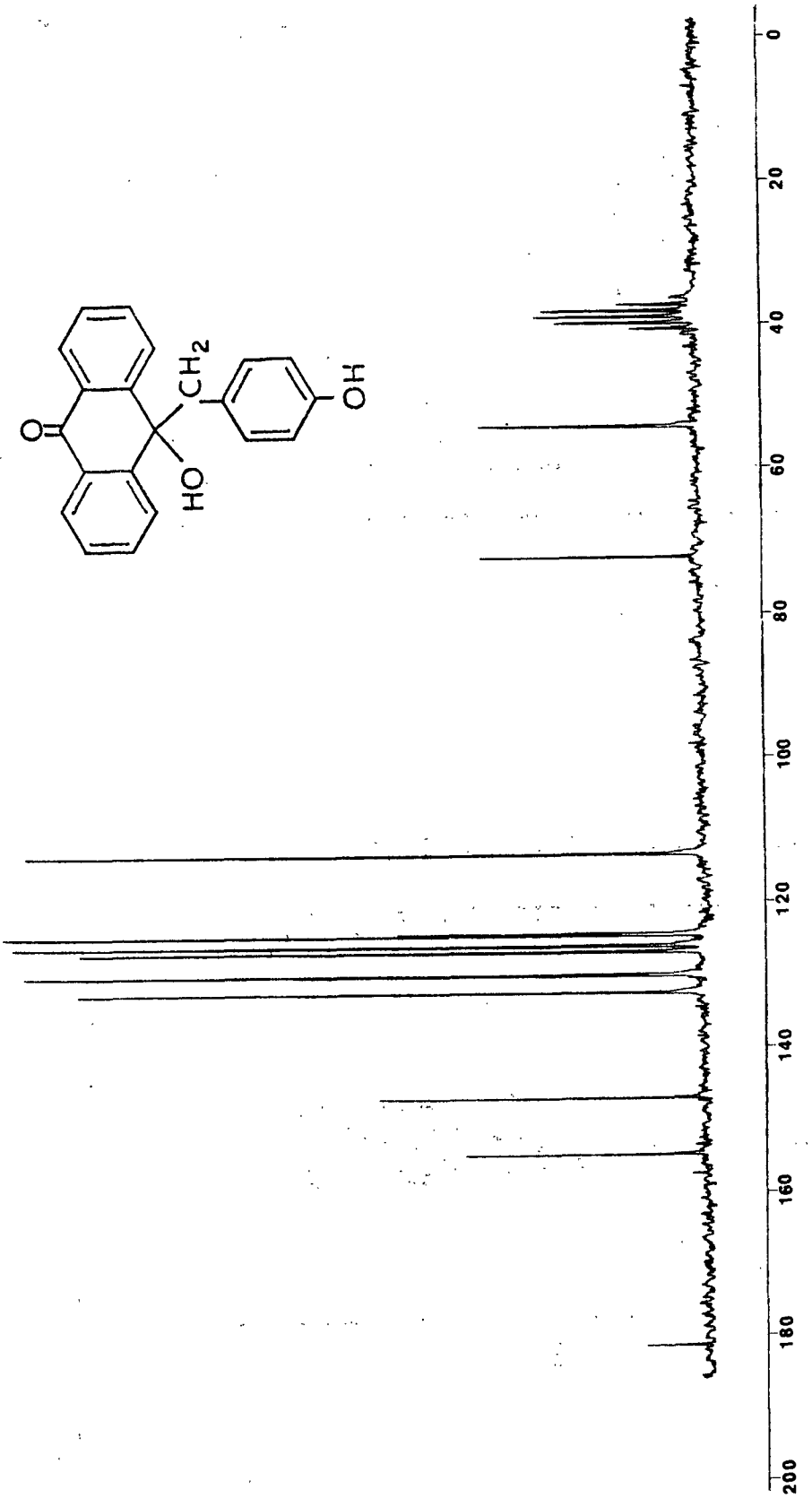


Figure 33. ^{13}C-NMR Spectrum of 10-Hydroxy-10-(4'-hydroxybenzyl)-9(10H)-anthracenone in DMSO. The Spectrum was Taken in a Decoupled Mode (C-H Coupling Disallowed). Detailed Assignment are Given in Table IV.

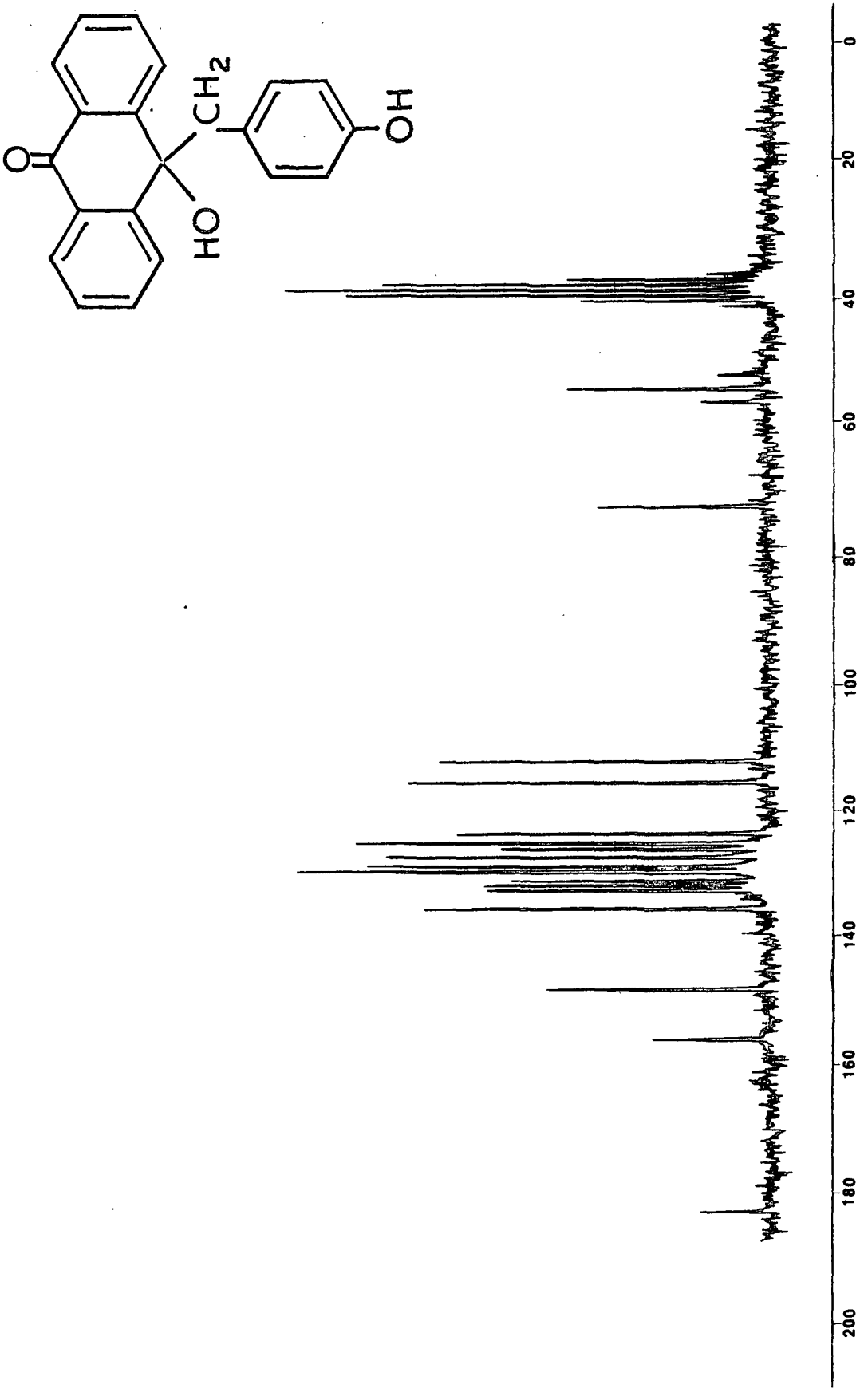


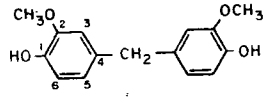
Figure 34. ^{13}C-NMR of 10-Hydroxy-10-(4'-hydroxybenzyl)-9(10H)-anthracenone in DMSO. The Off-resonance Mode Allows C-H Coupling.

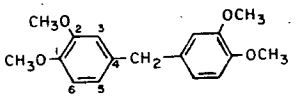
APPENDIX IV

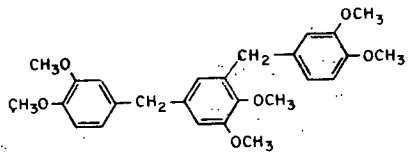
SUPPORTING NMR AND ELEMENTAL ANALYSES FOR SELECTED COMPOUNDS PREPARED OR ISOLATED DURING THE COURSE OF THIS STUDY

TABLE VI

NMR ($CDCl_3$) ASSIGNMENTS FOR VANILLYL ALCOHOL CONDENSATION PRODUCTS[a]





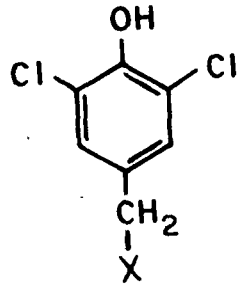


^{1}H-NMR		^{13}C-NMR		^{1}H-NMR		^{13}C-NMR		^{1}H-NMR	
Aryl	6.6-6.8 (m)	C_1	143.7 (s)	Aryl	6.7-6.9 (m)	C_1	148.0 (s)	Aryl	6.5-6.8 (m)
OH	5.63 (s)	C_2	146.3 (s)	OCH	3.84 (s), 3.81 (s)	C_2	149.6 (s)	OCH_3	3.65-3.85[c]
OCH_3	3.78 (s)	C_3	111.4 (d)[b]	CH_2	3.88 (s)	C_3	112.3 (d)[b]	CH_2	3.88 (s)
CH_2	3.81 (s)	C_4	133.2 (s)			C_4	136.5 (s)		
		C_5	121.3 (d)			C_5	120.8 (d)		
		C_6	114.1 (d)[b]			C_6	111.4 (d)[b]		
		CH_2	41.2 (t)			CH_2	41.0 (t)		
		CH_3	55.9 (q)			CH_3	56.0 (q)		

[a] Units are given in PPM (δ) relative to TMS = 0.
[b] Assignments could be interchanged.
[c] Several signals were in this region.

TABLE VII

^{1}H-NMR ASSIGNMENTS FOR 3,5-DICHLORO-4-HYDROXYLBENZYL DERIVATIVES[a]

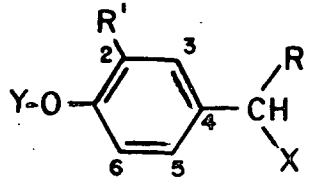


	X = H	X = OH	X = Cl	X = OMe	X = 
Text no.	35	36	28	31	30
Solvent	$CDCl_3$	$CDCl_3$	$CDCl_3$	$CDCl_3$	DMSO
Aryl-OH	5.67 (s)	3.2-4.7[b]	5.86 (s)	5.91 (s)	10.60 (s)
Aryl-H	7.02 (s)	7.20 (s)	7.27 (s)	7.25 (s)	7.78 (s)
Benzyl	2.22 (s)	4.51 (s)	4.44 (s)	4.33 (s)	5.84 (s)
Other		OH 3.2-4.7[b]		Me 3.36 (s)	ortho 9.34 (d)[c]
					meta 8.17 (t)[c]
					para 8.62 (t)[c]

[a] Values are in δ units relative to TMS = 0.
[b] Very broad signal.
[c] J = 7-8 Hz.

TABLE VIII

^{1}H-NMR ASSIGNMENTS AND ELEMENTAL ANALYSES OF SOME QUINONEMETHIDE PRECURSORS [a,b]

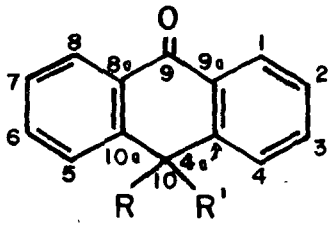


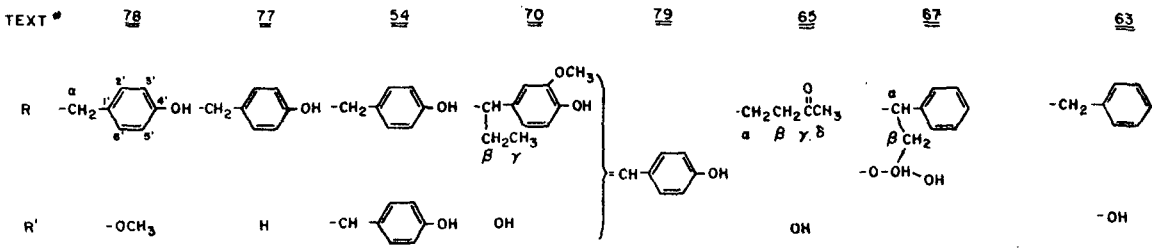
Text No.	Solvent	X	Y	R	R^1	C-6	C-5	C-3	C-d	Calculated (Found)[e] %C	%H
25	$CDCl_3$	Cl	$COCH_3$	H	H					--	--
			2.27 (s)		7.05 (d)		7.38 (d)		4.51 (s)		
27	$CDCl_3$	Cl	$COCH_3$	H	OCH_3					55.94 (56.03)	5.13 (5.14)
			2.30 (s)		3.84 (s)		6.7-6.9 (m)		4.56 (s)		
26	$CDCl_3$	OCH_3	H	H	H					--	--
		3.37 (s)	5.91 (s)		6.74 (d)		7.18 (d)		4.38 (s)		
86	DMSO	OH	H	CH_3	OCH_3					--	--
		4.94 (d)[c]	8.68 (s)	1.27 (d)	3.74 (s)		6.7-6.9 (m)		4.5 (d of q)[c]		
83	$CDCl_3$	Cl	$COCH_3$	CH_3	OCH_3					57.77 (58.18)	5.69 (5.87)
			2.25 (s)	1.80 (d)	3.79 (s)	7.07 (s)		7.22 (s)	5.23 (q)		
68	$CDCl_3$	OH	H	CH_2CH_3	OCH_3					--	--
		1.89 (s)	5.63 (s)	1.73 (m) 0.90 (t)	3.38 (s)		6.7-6.9 (m)		4.51 (t)		
69	$CDCl_3$	Cl	$COCH_3$	CH_2CH_3	OCH_3					59.38 (59.65)	6.19 (6.24)
			2.28 (s)	2.06 (p)[d] 1.00 (t)	3.81 (s)		6.9-7.0 (m)		4.74 (t)		

[a] Values are in δ units relative to TMS = 0.
[b] The coupling constants, J, were all in the 7-9 Hz range unless noted otherwise.
[c] Doublet has J = 4Hz.
[d] p = pentet.
[e] Analyses are only given for those compounds which have not been reported in the literature.

TABLE IX

^{13}C-NMR (DMSO) ASSIGNMENTS FOR SELECTED ANTHRAHYDROQUINONE AND ANTHRONE ADDITION PRODUCTS[a]



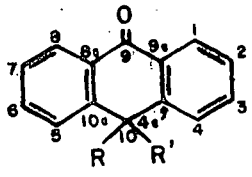


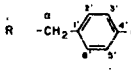
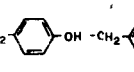
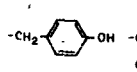
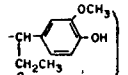
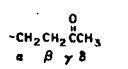
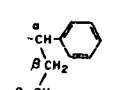
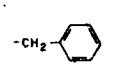
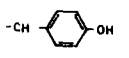
Positions	PPM	PPM[b]	PPM	PPM[b]	PPM[b]	PPM	PPM[b]	PPM[b,d]
C_1, C_8	127.0 (d)	128.4	129.0 (d)			127.4 (d)		127.7
C_2, C_7	126.2 (d)	126.5	127.2 (d)			126.2 (d)		126.2
C_3, C_6	132.8 (d)	132.2 (d)	133.7 (d)		132.6 (d) 134.2 (d)	133.3 (d)		133.0 (d)
C_4, C_5	124.7 (d)	125.6	126.4 (d)			125.6 (d)		125.7
C_{8a}, C_{9a}	127.5 (d)	131.5 (s)	132.3 (s)		129.3 (s) 131.2 (s)	129.7 (s)		131.0 (s)
C_{4a}, C_{10a}	147.3 (s)	143.7 (s)	146.8 (s)	144.5 (s) 144.7 (s)	139.8 (s) 135.8 (s)	147.7 (s)	147.6 143.7	146.3 (s)
C_9	181.5 (s)	182.6 (s)	183.1 (s)	181.7 (s)	183.0 (s)	182.6 (s)	182.5	182.4
C_{10}	72.5 (s)	43.3 (d)	50.0 (s)	74.7 (s)		70.5 (s)	87.2, 85.7[c]	73.8 (s)
C-α	54.4 (t)	46.6 (t)	48.7 (t)	63.0 (d)		42.5 (t)	59.4, 61.2[c]	55.4 (t)
C-β	--	--	--	21.6 (t)	--	37.7 (t)	37.5	--
C-γ	--	--	--	12.6 (q)	--	206.4 (s)	98.6, 100.0[c]	--
C-δ	--	--	--	--	--	29.3 (q)	--	--
C_1'	125.2 (s)	128.3 (s)	127.7 (s)			--		134.2 (s)
C_2'	130.3 (d)	129.8	130.5 (d)	114.1 (d)	130.6 (d)	--		130.0
C_6'	130.3 (d)	129.8	130.5 (d)		130.6 (d)	--		130.0
C_3'	113.6 (d)	113.8 (d)	114.2 (d)	149.2 (s)	115.2 (d)	--		127.2
C_5'	113.6 (d)	114.6 (d)	114.2 (d)	114.1 (d)	115.2 (d)	--		127.2
C_4'	155.1 (s)	155.1 (s)	155.1 (s)	145.9 (s)	157.3 (s)	--		126.5
Methoxy	49.3 (q)	--	--	55.0 (s)	--	--	--	--

[a] Values are in PPM relative to TMS = 0.
[b] The lack of assignment for the peak position or splitting was due to the complexity of aromatic region, which was either a result of overlapping signals or disymmetry of the molecule or both.
[c] This compound is a mixture of stereoisomers; the first value of the two assignments represents the more intense peak.
[d] The aromatic assignments are quite tentative in this case.

TABLE X

^{1}H-NMR (DMSO) ASSIGNMENTS AND ELEMENTAL ANALYSES FOR SELECTED ANTHRAHYDROQUINONE AND ANTHRONE ADDITION PRODUCTS[a]



TEXT #	78	77	54	70	79	65	67	63
R								
R'	-OCH$_3$	H		OH		OH		-OH
Positions	PPM	PPM	PPM	PPM	PPM	PPM	PPM[d]	PPM[e]
C_1, C_8	7.5-8.0 (m)	7.95 (d)	8.29 (d)	7.4-8.0	7.4-8.3 (m)	7.4-8.1 (m)	8.2 (m)	7.2-8.0 (m)
C_2, C_7		7.4-7.6 (m)	7.84 (t)				7.3-7.8 (m)	
C_3, C_6			7.42 (t)					
C_4, C_5			7.88 (d)					
C_{10}	--	4.72 (t)[b]	--	--	--	--	--	--
C-α	3.05 (s)	3.12 (d)[b]	3.67 (s)	C	7.4-8.3 (m)	2.0 (m)	2.29 (d of d)	3.16 (s)
C-β	--	--	--	1.10 (m)	--		2.74 (d of t)	--
C-γ	--	--	--	0.55 (t)	--	--	3.80 (d of d)	--
C-δ	--	--	--	--	--	1.82 (s)	6.34 (d)	--
C_2'	6.18 (d)	6.28 (d)	6.13 (d)	5.34 (s)	7.24 (d)	--	6.1 (d)	6.08 (d)
C_6'				6.19 (d)		--		
C_3'	5.74 (d)	5.98 (d)	6.00 (d)	--	6.75 (d)	--	6.9 (m)	6.8-7.0 (m)
C_5'				5.34 (d)		--		
C_4'	--	--	--	--	--	--		
Aryl-OH	9.00 (s)	9.03 (s)	9.03 (s)	8.55 (s)	9.77 (s)	--	--	--
Aliph.-OH	--	--	--	6.34 (s)	--	6.34 (s)		2.62 (s)
Methoxy	3.36 (s)	--	--	3.24 (s)	--	--	--	--
ELEMENTAL ANALYSES								
Calc. % C	80.00	84.00	82.76	--	84.60	77.10	80.70	84.00
Found % C	73.69	81.86	82.28	--	83.76	76.06	80.39	83.95
Calc. % H	5.45	5.33	5.42	--	4.70	5.83	5.26	5.33
Found % H	5.13	5.53	5.61	--	4.84	5.71	5.31	5.32

[a] Values are in δ units relative to TMS = 0; the J values for split signals are in the 7-9 Hz range unless noted otherwise.

[b] J ≈ 5 Hz.

[c] Unable to locate this singal; it may be under the strong 3.32 (H_2O) and 3.24 (OCH_3) signals or be one of the small signals in 2.1-2.9 range.

[d] The α,β and γ protons comprise a ABB' system with apparent coupling constants for the major isomer of: AB = 13 Hz, AB' = 7 Hz, BB' = 13 Hz, BC = 6 Hz and B'C = 0 Hz. The relationships and peak assignments protons and C_2', C_6' ortho aromatic protons were arrived at by decoupling techniques. The OH proton was not seen; there was a large amount of water in our DMSO solvent which may have masked the signal. A spectrum in $CDCl_3$ also did not pinpoint the OH signal. An IR spectrum clearly shows no CHO and the existence of an alcohol.

[e] Run with $CDCl_3$ as the solvent.

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